

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 March 2004 (04.03.2004)

PCT

(10) International Publication Number
WO 2004/018095 A1

(51) International Patent Classification⁷: **B01J 23/86**,
23/26, C07C 17/20, 19/12

(21) International Application Number:
PCT/US2003/026327

(22) International Filing Date: 21 August 2003 (21.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/405,221 22 August 2002 (22.08.2002) US

(71) Applicant (for all designated States except US): **E.I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **NAPPA, Mario, J.** [US/US]; 3 Oakridge Court, Newark, DE 19711 (US). **RAO, Velliyur, Nott, Mallikarjuna** [US/US]; 1 Georgetown Avenue, Wilmington, DE 19809 (US). **ROSENFELD, H., David** [US/US]; 1927 Susquehannock Drive, Drumore, PA 17518 (US). **SUBRAMONEY,**

Shekhar [IN/US]; 425 Stella Drive, Hockessin, DE 19707 (US). **SUBRAMANIAN, Munirpallam, A.** [US/US]; 20 Pratt Lane, Kennett Square, PA 19348 (US). **SIEVERT, Allen, C.** [US/US]; 215 Rhett Lane, Elkton, MD 21921 (US).

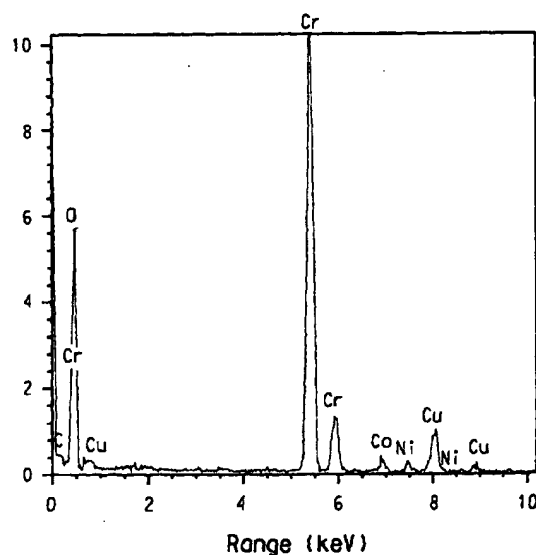
(74) Agent: **HEISER, David, E.**; E.I. Du Pont De Nemours and Company, 4417 Lancaster Pike, Wilmington, DE 19805 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,

[Continued on next page]

(54) Title: NICKEL-SUBSTITUTED AND MIXED NICKEL-AND-COBALT-SUBSTITUTED CHROMIUM OXIDE COMPOSITIONS, THEIR PREPARATION, AND THEIR USE AS CATALYSTS AND CATALYST PRECURSORS



(57) Abstract: A crystalline alpha-chromium oxide where from about 0.05 atom % to about 2 atom % of the chromium atoms in the alpha-chromium oxide lattice are substituted by nickel atoms, and optionally, additional chromium atoms in the alpha-chromium oxide lattice are substituted by trivalent cobalt atoms (provided that the total amount of the nickel atoms and the trivalent cobalt atoms in the alpha-chromium oxide lattice is no more than 6 atom %) is disclosed. Also disclosed is a chromium-containing catalyst composition comprising as a chromium-containing component the crystalline substituted alpha-chromium oxide; and a method for preparing a composition comprising the crystalline substituted alpha-chromium oxide. The method comprises (a) co-precipitating a solid by adding ammonium hydroxide to an aqueous solution of a soluble divalent nickel salt, a soluble trivalent chromium salt, and optionally, a soluble divalent or trivalent cobalt salt, that contains at least three moles of nitrate per mole of chromium in the solution, has a nickel concentration of from about 0.05 mole % to about 2 mole % of the total of nickel, chromium, and cobalt in the solution, and has a combined concentration of nickel and cobalt of no more than 6 mole % of the total of nickel, chromium, and cobalt in the solution; and after at

least three moles of ammonium per mole of chromium has been added to the solution; (b) collecting the co-precipitated solid formed in (a); (c) drying the collected solid; and (d) calcining the dried solid. Also disclosed is a chromium-containing catalyst composition comprising a chromium-containing component prepared by treating said crystalline substituted alpha-chromium oxide with a fluorinating agent; and a process for changing the fluorine distribution (i.e., content and/or arrangement) in a hydrocarbon or halogenated hydrocarbon in the presence of a catalyst. The process involves using as the catalyst a composition comprising the crystalline substituted alpha-chromium oxide and/or the treated substituted alpha-chromium oxide.



SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

TITLE

NICKEL-SUBSTITUTED AND MIXED NICKEL- AND COBALT-SUBSTITUTED CHROMIUM OXIDE COMPOSITIONS, THEIR PREPARATION, AND THEIR USE AS CATALYSTS AND CATALYST PRECURSORS

FIELD OF THE INVENTION

This invention relates to chromium-containing compositions and their preparation and use for the catalytic processing of hydrocarbons and/or halogenated hydrocarbons.

BACKGROUND

It is well known that $\alpha\text{-Cr}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ have in common the structure of $\alpha\text{-Al}_2\text{O}_3$ (corundum) with the M^{+3} ions occupying octahedral sites in the hexagonally close-packed oxide lattice. In contrast, NiO and CoO have distorted cubic lattices while Co_3O_4 has a normal spinel structure. These basic structures are described in standard treatises; see, for example, pages 538, 543-545, and 550 of *Structural Inorganic Chemistry* by A. F. Wells, 5th ed. Clarendon Press, Oxford, UK (1986). γ -Chromium oxide ($\text{CrO}_{2.44}$) is described in Wilhelmi, *Acta Chemica Scandinavica*, Vol. 22, pages 2565-2573 (1968).

Numerous mixed metal oxides have been prepared in which the cation sites of the lattice are occupied by different metal ions. For example, solid solutions of the type $(\text{Cr}_m\text{Fe}_{1-m})_2\text{O}_3$ are known where $0 < m < 1$. These materials have been prepared by standard ceramic or sol-gel techniques as described by Music, et al. in *J. Materials Science*, Vol. 31, pages 4067-4076 (1996) and by Bhattacharya, et al. in *J. Materials Science*, Vol. 32, pages 577-560 (1997).

Mixed Cr-Ni oxides are known (see e.g., Chamberland and Cloud, *J. of Applied Physics*, Vol. 40, pages 434-435 (1969) where NiCrO_3 which has a corundum-type structure is discussed; Muller, et. al., *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, Vol. 130, pages 112-120 (1969); Prince, *J. of Applied Physics*, Vol. 32, pages 68S-69S (1961); and Nowotny et al., *Bulletin of the Polish Academy of Sciences, Chemistry*, Vol. 33, pages 111-119 (1985). Mixed Cr-Co oxides having a spinel structure are known (see e.g., Bracconi et al. in *Ann. Chim. Fr.*, Vol. 4, pages 331-338 (1979) and Hanck and Laitinen in *J. Inorg. Nucl. Chem.*, Volume 33, pages 63-73 (1971)).

CrCoO₃ is referenced as an interconnector material in a fuel cell assembly (see Chem. Abs. 118:9397). Various mixed metal oxides

containing cobalt and chromium are also disclosed in Castiglioni, et al., *J. Solid State Chemistry*, Vol. 152, 526-532 (2000); Nowotny et al., *J. Am. Ceram. Soc.*, Vol. 65, pages 192-196 (1982); and Zhang et al., *Journal of Power Sources*, Vol. 83, pages 121-127 (1999).

5 Certain metal oxides are used as catalysts and/or catalyst precursors in the manufacture of fluorinated hydrocarbons. Chromium(III) oxide in particular is useful as it has been found that it may be fluorinated by HF at elevated temperature to give a mixture of chromium fluoride and chromium oxyfluoride species which are active catalysts for conversion of
10 C-Cl bonds to C-F bonds in the presence of HF. This conversion of C-Cl bonds to C-F bonds by the action of HF, known generally as halogen exchange, is a key step in many fluorocarbon manufacturing processes.

Chromium oxide compositions useful as catalyst precursors may be prepared in various ways or may take various forms. Chromium oxide
15 suitable for vapor phase fluorination reactions may be prepared by reduction of Cr(VI) trioxide, by dehydration of Guignet's green, or by precipitation of Cr(III) salts with bases (see U. S. Patent No. 3,258,500). Another useful form of chromium oxide is hexagonal chromium oxide hydroxide with low alkali metal ion content as disclosed in U. S. Patent
20 No. 3,978,145. Compounds such as MF_4 ($M = Ti, Th, Ce$), MF_3 ($M = Al, Fe, Y$), and MF_2 ($M = Ca, Mg, Sr, Ba, Zn$) have been added to hexagonal chromium oxide hydroxide to increase catalyst life as disclosed in U.S. Patent No. 3,992,325. A form of chromium oxide that is a precursor to a particularly active fluorination catalyst is that prepared by pyrolysis of
25 ammonium dichromate as disclosed in U. S. Patent No. 5,036,036.

The addition of other compounds (e.g., other metal salts) to supported and/or unsupported chromium-based fluorination catalysts has been disclosed. Australian Patent Document No. AU-A-80340/94 discloses bulk or supported catalysts based on chromium oxide (or oxides
30 of chromium) and at least one other catalytically active metal (e.g., Mg, V, Mn, Fe, Co, Ni, or Zn), in which the major part of the oxide(s) is in the crystalline state (and when the catalyst is a bulk catalyst, its specific surface, after activation with HF, is at least $8 \text{ m}^2/\text{g}$). The crystalline phases disclosed include Cr_2O_3 , CrO_2 , $NiCrO_3$, $NiCrO_4$, $NiCr_2O_4$,
35 $MgCrO_4$, $ZnCr_2O_4$ and mixtures of these oxides. Australian Patent Document AU-A-29972/92 discloses a mass catalyst based on chromium and nickel oxides in which the Ni/Cr atomic ratio is between 0.05 and 5. U.S. Patent Application Publication No. US2001/0011061 A1 discloses

- chromia-based fluorination catalysts (optionally containing Mg, Zn, Co, and Ni) in which the chromia is at least partially crystalline. Fluorinated catalysts containing cobalt and chromium in combination (e.g. impregnated on a support) are among those disclosed in U.S. Patent No. 5,185,482. U.S. Patent No. 5,559,069 discloses homogeneously dispersed multiphase catalyst compositions characterized by dispersed phases of certain divalent metal fluorides (certain fluorides of Mn, Co, Zn, Mg, and/or Cd) and certain trivalent metal fluorides (fluorides of Al, Ga, V, and/or Cr).
- There remains a need for halogen exchange catalysts that can be used for processes such as the selective fluorination and chlorofluorination of saturated and unsaturated hydrocarbons, hydrochlorocarbons, hydrochlorofluorocarbons, and chlorofluorocarbons, the fluorination of unsaturated fluorocarbons, the isomerization and disproportionation of fluorinated organic compounds, the dehydrofluorination of hydrofluorocarbons, and the chlorodefluorination of fluorinated hydrocarbons.

SUMMARY OF THE INVENTION

- This invention provides a crystalline alpha-chromium oxide where from about 0.05 atom % to about 2 atom % of the chromium atoms in the alpha-chromium oxide lattice are substituted by nickel atoms, and optionally, additional chromium atoms in the alpha-chromium oxide lattice are substituted by trivalent cobalt atoms, provided that the total amount of the nickel atoms and the trivalent cobalt atoms in the alpha-chromium oxide lattice is no more than 6 atom %.

This invention also provides a chromium-containing catalyst composition comprising as a chromium-containing component said crystalline substituted alpha-chromium oxide.

- This invention also provides a method for preparing a composition comprising said crystalline substituted alpha-chromium oxide. The method comprises (a) co-precipitating a solid by adding ammonium hydroxide (aqueous ammonia) to an aqueous solution of a soluble divalent nickel salt, a soluble trivalent chromium salt, and optionally, a soluble divalent or trivalent cobalt salt, that contains at least three moles of nitrate (i.e., NO_3^-) per mole of chromium (i.e., Cr^{+3}) in the solution, has a nickel concentration of from about 0.05 mole % to about 2 mole % of the total of nickel, chromium, and cobalt (if present) in the solution, and has a combined concentration of nickel and cobalt (if present) of no more than 6 mole % of

- the total of nickel, chromium, and cobalt (if present) in the solution; and after at least three moles of ammonium (i.e., NH_4^+) per mole of chromium (i.e., Cr^{+3}) has been added to the solution; (b) collecting the co-precipitated solid formed in (a); (c) drying the collected solid; and (d)
- 5 calcining the dried solid.

This invention also provides a chromium-containing catalyst composition comprising a chromium-containing component prepared by treating said crystalline substituted alpha-chromium oxide with a fluorinating agent (e.g., hydrogen fluoride).

- 10 This invention also provides a process for changing the fluorine distribution (i.e., content and/or arrangement) in a hydrocarbon or halogenated hydrocarbon in the presence of a catalyst. The process is characterized by using as the catalyst a composition comprising at least one chromium-containing component selected from the group consisting of
- 15 said crystalline substituted alpha-chromium oxides and said treated substituted alpha-chromium oxides.

BRIEF DESCRIPTION OF THE DRAWINGS

- Figure 1 represents an energy dispersive spectroscopy spectrum for a sample of mixed nickel- and cobalt-substituted alpha-chromium oxide
- 20 nominally containing 3 atom % cobalt and 2 atom % nickel.

Figure 2 represents an energy dispersive spectroscopy spectrum for a sample of alpha-chromium oxide without nickel or cobalt substitution.

Figure 3 represents an energy dispersive spectroscopy spectrum for a sample of nickel chromium spinel.

- 25 Figure 4 represents an energy dispersive spectroscopy spectrum for a sample of cobalt chromium spinel.

Figure 5 represents an energy dispersive spectroscopy spectrum for a sample of nickel-substituted alpha-chromium oxide nominally containing 2 atom % nickel.

- 30 Figure 6 represents a plot of the radial distribution function (i.e., the probability of finding an atom at a certain distance, r , from a central atom) associated with the local atomic structure around (A) a nickel central atom in NiO , (B) nickel in a sample of NiCr_2O_4 , (C) a chromium central atoms in $\alpha\text{-Cr}_2\text{O}_3$, and (D) nickel in a sample of the mixed nickel- and cobalt-
- 35 substituted alpha-chromium oxide nominally containing 3 atom % cobalt and 2 atom % nickel.

Figure 7 represents a plot of the radial distribution function associated with the local atomic structure around (A) a cobalt central atom

in CoO, (B) a cobalt central atom in Co_3O_4 , (C) a chromium central atom in $\alpha\text{-Cr}_2\text{O}_3$, and (D) a cobalt atom in a sample of the mixed nickel- and cobalt-substituted α -chromium oxide nominally containing 3 atom % cobalt and 2 atom % nickel.

5 Figure 8 represents a plot of the radial distribution function associated with the local atomic structure around (A) a nickel central atom in NiO, (B) nickel in a sample of NiCr_2O_4 , (C) a chromium central atom in $\alpha\text{-Cr}_2\text{O}_3$, and (D) a nickel atom in a sample of nickel-substituted α -chromium oxide nominally containing 2 atom % nickel.

10 DETAILED DESCRIPTION

New compositions of this invention comprise substituted α -chromium oxide containing nickel, or both nickel and cobalt, which retains the corundum structure. This invention includes a catalytic composition comprising said crystalline substituted $\alpha\text{-Cr}_2\text{O}_3$. The nickel content of the substituted α -chromium oxide is from about 0.05 atom % to about 2 atom % of the total of the nickel, chromium, and cobalt (if present) in the α -chromium oxide. The total of the nickel and cobalt in the α -chromium oxide is no more than 6 atom % of the total of the nickel, chromium, and cobalt. The crystalline substituted α -chromium oxides have the general formula $\alpha\text{-Ni}_x\text{Co}_y\text{Cr}_{2-x-y}\text{O}_3$ where x is 0.001 to 0.04 and y is 0 to 0.12 - x.

The compositions of the present invention may be prepared by the method described above using co-precipitation. In the typical co-precipitation technique, an aqueous solution of nickel(II) and chromium(III) salts, and optionally cobalt(II) or cobalt(III) salts, is prepared. The relative concentrations of nickel(II), cobalt, and chromium(III) salts in the aqueous solution is dictated by the bulk mole percent nickel and cobalt relative to chromium desired in the final catalyst. The concentration of chromium(III) in the aqueous solution is typically in the range of from 0.3 to 3 molar (moles per liter) with 0.75-1.5 molar being a preferred concentration. Chromium(III) salts suitable for preparation of the aqueous solution are the nitrate, sulfate, acetate, formate, oxalate, phosphate, bromide, and chloride and various hydrated forms of these salts. Other chromium(III) salts that are useful for the preparation of the aqueous solutions include hexacoordinate complexes of the formula $[\text{CrL}_{6-z}\text{A}_z]^{+3-z}$ where each L is a neutral (i.e., uncharged) ligand selected from the group consisting of H_2O , NH_3 , C1-C4 primary, secondary, or tertiary organic amines, a C1-C4 alkyl nitriles, or pyridine, where each A is an anionic ligand selected from the

group consisting of fluoride, chloride, bromide, iodide, hydroxide, nitrite, and nitrate, and where z has a value of from 0 to 3 inclusive. Included are neutral bidentate ligands such as ethylene diamine which are equivalent to two L in that they may occupy two coordination sites. Also included are
5 anionic bidentate ligands such as C₁-C₄ carboxylate which may occupy two coordination sites. Also included are dianionic ligands such as sulfate which are equivalent to two A ligands and may occupy more than one coordination site.

Salts containing alkali metals such as chromium potassium sulfate
10 are not preferred because the presence of alkali metals can hinder catalyst activity (see U. S. Patent 4,843,181). Chromium(VI) precursors, such as CrO₃, though not preferred, may be used but require reduction to Cr(III) with a compound such as ethanol before precipitation.

Chromium(III) nitrate, or its hydrated forms such as
15 [Cr(NO₃)₃(H₂O)₉], are the most preferred chromium(III) salt for preparation of said aqueous solution.

Nickel(II) salts suitable for preparation of the aqueous solution are the nitrate, acetate, acetylacetonate, sulfate, formate, oxalate, bromide, chloride, and fluoride and various hydrated forms of these salts. Nickel(II)
20 nitrate hydrate (e.g., [Ni(NO₃)₂(H₂O)₆]) is the most preferred nickel(II) salt.

Cobalt(II) salts suitable for preparation of the aqueous solution are the nitrate, sulfate, formate, oxalate, bromide, and chloride and various hydrated forms of these salts. Salts containing alkali metals such as cobalt potassium bis(sulfate) are not preferred because the presence of
25 alkali metals can hinder catalyst activity. Cobalt(II) nitrate hydrate (e.g., [Co(NO₃)₂(H₂O)₆]) is the most preferred cobalt(II) salt.

Cobalt(III) salts that are useful for the preparation of the aqueous solutions include hexacoordinate complexes of the formula [CoL_{6-z}A_z]^{+3-z} where each L is a neutral (i.e., uncharged) ligand selected from the group
30 consisting of H₂O, NH₃, C₁-C₄ primary, secondary, or tertiary organic amine, a C₁-C₄ alkyl nitrile, or pyridine, where each A is an anionic ligand selected from the group consisting of fluoride, chloride, bromide, iodide, hydroxide, nitrite, and nitrate, and where a has a value of from 0 to 3 inclusive. Included are neutral bidentate ligands such as ethylene diamine
35 which are equivalent to two L in that they may occupy two coordination sites. Also included are anionic bidentate ligands such as C₁-C₄ carboxylate which may occupy two coordination sites. Also included are dianionic ligands such as sulfate which are equivalent to two A ligands and

may occupy more than one coordination site. Preferred cobalt(III) starting materials are hexammine salts (e.g., $[\text{Co}(\text{NH}_3)_6]^{+3}$ where the counter ion is chloride or nitrate. Hexaamminecobalt(III) chloride (e.g., $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$) is the most preferred cobalt(III) salt.

- 5 The aqueous solution of the nickel(II) and chromium(III) salts, and optionally cobalt(II) or cobalt(III) salts, may then be evaporated either under vacuum or at elevated temperature to give a solid which is then calcined.

- 10 Preferably, however, the aqueous solution of nickel(II) and chromium(III) salts, and optionally cobalt salts, is then treated with a base such as ammonium hydroxide (aqueous ammonia) to precipitate the nickel and chromium, and optionally cobalt, as the hydroxides. Bases containing alkali metals such as sodium or potassium hydroxide or the carbonates may be used but are not preferred. The addition of ammonium hydroxide to the aqueous solution of nickel(II) and chromium(III) salts, and optionally cobalt salt(s), is typically carried out gradually over a period of 1 to 12 hours. The pH of the solution is monitored during the addition of base. The final pH is typically in the range of 6.0 to 11.0, preferably from about 7.5 to about 9.0, and most preferably from about 8.0 to 8.7. The precipitation of the nickel hydroxide/cobalt hydroxide/chromium hydroxide mixture is typically carried out at a temperature of about 15°C to about 60°C, preferably from about 20°C to about 40°C. After the ammonium hydroxide is added, the mixture is typically stirred for up to 24 hours.

- 20 Of note are preparations where excess ammonium nitrate (i.e., more than three moles of ammonium nitrate per mole of chromium) is present in the aqueous solution. For example, in addition to the ammonium nitrate already present from reaction of ammonium hydroxide with chromium nitrate, from about 0.1 mole to about 7.0 moles of additional ammonium nitrate per mole of chromium may be added to the solution before, during, or after the co-precipitation of the compositions. Surprisingly, we have found that addition of ammonium nitrate to the precipitated mixture of nickel and chromium, and optionally cobalt, hydroxides prior to the dehydration step decreases the particle size of the $\alpha\text{-Ni}_x\text{Co}_y\text{Cr}_{2-x-y}\text{O}_3$ phase which in turn increases the surface area of that phase and the activity of the catalyst.

35 After the ammonium nitrate is added to the mixture, it is stirred for about 0.5 to ten hours, preferably one to five hours at a temperature of

from about 20°C to about 60°C. The mixture is then dried and calcined as indicated below.

Other agents that serve this purpose include aqueous hydrogen peroxide (1% to 30% solutions), ozone, peroxy acids such as peroxyacetic acid, and ammonium persulfate. Agents such as halogens may be used but are not preferred. Agents containing alkali metals such as potassium persulfate or sodium perborate may also be used but are not preferred.

After the precipitation of the mixture of nickel, chromium, and optionally cobalt, hydroxides is complete, and the ammonium nitrate or other agents added if desired, the mixture is dried by evaporation.

Optionally, the precipitated mixture of metal hydroxides may be collected and, if desired, washed with deionized water before drying. This may influence the activity of the catalyst.

After the mixture of metal hydroxides has been dried, the nitrate salts are then decomposed by heating the solid from about 250°C to about 350°C. The resulting solid is then calcined at temperature of from about 375°C to about 1000°C, preferably from about 400°C to about 600°C. The calcination temperature can influence the activity of the catalysts and, in turn, the product distribution when the catalysts are used to change the fluorine distribution in hydrocarbons and halogenated hydrocarbons (see Examples 9, 10, 11, and 12).

The calcination is preferably carried out in the presence of oxygen, most preferably in the presence of air.

The metal oxide compositions of this invention may be characterized by well-established analytical techniques including X-Ray absorption spectroscopy (XAS), X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDS). EDS is an analytical tool available in conjunction with scanning or analytical TEM.

After calcination, the resulting nickel-substituted, and optionally cobalt-substituted, crystallites are not visually distinguishable from α -Cr₂O₃ by TEM. Furthermore, X-ray and electron diffraction studies are entirely consistent with the α -Cr₂O₃ structure with some lattice contraction or expansion proportional to the amount of Ni and, if present, Co(III), substituted for Cr(III) in the structure. The compositions are therefore concluded to have the general formula α -Ni_xCo_yCr_{2-x-y}O₃ where x is from 0.001 to 0.04 and y is from 0 to 0.12 - x.

The presence of various nickel/chromium and nickel/cobalt/chromium compositions of this invention is clearly indicated by elemental analysis using EDS. Figure 1 shows the EDS spectrum of a sample of a mixed nickel- and cobalt-substituted α -Cr₂O₃ nominally containing 2 atom % nickel and 3 atom % Co. For comparison, Figure 2 shows the EDS spectrum of α -Cr₂O₃ without nickel- or cobalt-substitution. Figures 3 and 4 show the EDS spectrum of commercially available nickel chromite, NiCr₂O₄, and cobalt chromite, CoCr₂O₄, respectively. Figure 5 shows the EDS spectrum of a sample of a nickel-substituted α -Cr₂O₃ nominally containing 2 atom % nickel. In each of these five figures, X-ray intensity, I, representing thousands of counts is plotted against energy level, E, representing thousands of electron volts (keV). Peaks in each plot correlate with the presence of certain elements.

The presence of nickel and cobalt are clearly indicated in the EDS spectrum in Figure 1, and the presence of nickel (but not cobalt) is clearly indicated in Figure 5, while the nickel and cobalt peaks are absent in Figure 2. The relative heights of 2:1 for the K α peaks of Cr (atomic mass 52) and Ni (atomic masses 58 and 60), respectively, in Figure 3, and the relative heights of 2:1 for the K α peaks of Cr and Co (atomic mass 59) in Figure 4, indicate that the EDS data are valid on a quantitative basis.

XAS and XRD data were obtained for a composition that was nominally 100% Cr (no cobalt added), for a composition that was nominally 95% Cr, 3% Co, and 2% Ni, for a composition that was nominally 98% Cr and 2% Ni, and for a composition that was nominally 95% Cr and 5% Ni. XAS and XRD analysis clearly show that the cobalt and nickel are substituted into α -Cr₂O₃.

XRD results for a composition that is nominally 2 atom % nickel, 3 atom % cobalt, and 95 atom % chromium are shown Table 1. Diffraction peaks having d-spacings of 3.1176, 1.9144, 1.3559, 1.2440, and 1.1076 are due to a silicon internal standard added to the sample for calibration of the diffractometer. All other diffraction peaks can be indexed to the α -Cr₂O₃ structure with a slightly reduced unit cell volume.

XRD results for a composition that is nominally 2 atom % nickel and 98 atom % chromium are shown Table 2. Diffraction peaks having d-spacings of 3.1336, 1.92, 1.6375, 1.3579, 1.246, and 1.1085 are due to a silicon internal standard added to the sample for calibration of the diffractometer. All other diffraction peaks can be indexed to the α -Cr₂O₃ structure with a slightly expanded unit cell volume.

TABLE 1

XRD Results for a Ni- and Co-Substituted α -Cr₂O₃
Composition that is Nominally 95 atom % Cr, 2 atom % Ni, and
3 atom % Co

5		<u>d (Angstroms)</u>	<u>Height</u>	<u>FWHM^a</u>
		3.6002	88	0.518
		3.1176	2932	0.173
		2.6432	219	0.522
10		2.4634	427	0.404
		2.2513	34	0.320
		2.1631	178	0.440
		1.9144	2767	0.200
		1.8075	134	0.543
15		1.6621	555	0.569
		1.6336	1672	0.235
		1.4571	110	0.525
		1.4243	256	0.594
		1.3559	474	0.256
20		1.2907	93	0.669
		1.2440	907	0.261
		1.2059	44	0.400
		1.1452	54	0.412
		1.1209	42	0.369
25		1.1076	1285	0.236

a. FWHM is full width at half maximum.

TABLE 2

XRD Results for a Ni-Substituted α -Cr₂O₃ Composition
that is Nominally 98 atom % Cr and 2 atom % Ni

30		<u>d (Angstroms)</u>	<u>Height</u>	<u>FWHM^a</u>
		3.6216	222	0.579
35		3.1336	1910	0.138
		2.6588	502	0.623
		2.4655	1056	0.435
		2.2546	125	0.355

TABLE 2 continued

	<u>d (Angstroms)</u>	<u>Height</u>	<u>FWHM^a</u>
5	2.1603	520	0.467
	1.92	1971	0.159
	1.8115	262	0.679
	1.6612	1406	0.524
	1.6375	1347	0.178
10	1.5738	110	0.482
	1.4571	276	0.6
	1.4566	250	0.742
	1.4237	650	0.61
	1.3579	388	0.157
15	1.2925	225	0.753
	1.246	801	0.138
	1.2329	174	0.689
	1.2074	135	0.635
	1.2025	139	0.617
20	1.1444	146	0.359
	1.1249	144	0.554
	1.1085	906	0.164
	1.1057	392	0.272

a. FWHM is full width at half maximum.

25 Figure 6, 7, and 8 show the radial distribution function (RDF) for several materials. The radial distribution function represents the probability of finding an atom a certain distance, r , from a central atom. These probabilities are weighted by factors that depend on the type of atom. Thus an RDF is a representation of local atomic structure around the central atom. An RDF is obtained by Fourier transform of the extended x-ray absorption fine structure (EXAFS) data, and may be represented by a plot of the dimensionless Fourier transform magnitude, F , versus the pair separation distance in angstroms. In simplified terms, one might view a peak in an RDF plot as indicative of a distance at which there is a coordination sphere around the central atom. A small difference is expected between the actual separation distance and the " r " shown in a plot when no correction is made to account for the phase shift on backscattering of excited electrons.

In Figure 6, F is plotted against the pair separation distance, r (shown in angstroms, uncorrected for phase shift) for each of four materials. Included in Figure 6 are curve (A) representing the local structure around nickel in NiO, curve (B) representing the local structure around nickel in NiCr_2O_4 , curve (C) representing the local structure around chromium in $\alpha\text{-Cr}_2\text{O}_3$, and curve (D) representing the local structure around nickel in a sample of a mixed nickel- and cobalt-substituted α -chromium oxide nominally containing 3 atom % cobalt and 2 atom % nickel. No spinel phase was detected by electron microscopy in this sample, so all the Ni and Co are considered to be associated with the $\alpha\text{-Cr}_2\text{O}_3$ phase, either as a separate metal oxide coating, or as a substitute for Cr in the $\alpha\text{-Cr}_2\text{O}_3$ lattice.

In Figure 7, F is plotted against the pair separation distance, r (shown in angstroms, uncorrected for phase shift) for each of four materials. Included in Figure 7 are curve (A) representing the local structure around cobalt in CoO, curve (B) representing the local structure around cobalt in Co_3O_4 , curve (C) representing the local structure around chromium in $\alpha\text{-Cr}_2\text{O}_3$, and curve (D) representing the local structure around cobalt in the same sample of mixed nickel- and cobalt-substituted α -chromium oxide shown in Figure 6 (nominally containing 3 atom % cobalt and 2 atom % nickel).

In Figure 8, F is plotted against the pair separation distance, r (shown in angstroms, uncorrected for phase shift) for each of the four materials. Included in Figure 8 are curve (A) representing the local structure around nickel in NiO, curve (B) representing the local structure around nickel in NiCr_2O_4 , curve (C) representing the local structure around chromium in $\alpha\text{-Cr}_2\text{O}_3$, and curve (D) representing the local structure around nickel in a sample of nickel-substituted α -chromium oxide nominally containing 2 atom % nickel. No spinel phase was detected by electron microscopy in this sample, so all the Ni is considered to be associated with the $\alpha\text{-Cr}_2\text{O}_3$ phase, either as a separate metal oxide coating, or as a substitute for Cr in the $\alpha\text{-Cr}_2\text{O}_3$ lattice.

The curve in Figure 6 representing the local structure around nickel in the mixed nickel- and cobalt-substituted α -chromium oxide and the curve in Figure 7 representing the local structure around cobalt in the same composition, indicate that the local atomic structure around Ni and Co in this sample bears no resemblance to that of expected common nickel and cobalt oxide phases, but is very similar to that of Cr in the $\alpha\text{-Cr}_2\text{O}_3$ phase.

Cr₂O₃ phase. A similar conclusion may be drawn by comparison of the curves in Figure 8; namely, that the local atomic structure around Ni in the Cr/Ni 98/2 sample bears no resemblance to that of expected common nickel oxide phase, but is very similar to that of Cr in the α -Cr₂O₃ phase.

5 Table 3 gives the unit cell parameters and the unit cell volume for unsubstituted alpha-chromium oxide as well as three substituted alpha-chromium oxide compositions. The change in unit cell volume may be understood in terms of differences in the ionic radii of the substituted metals. According to data presented by Shannon and Prewitt in *Acta*
 10 *Crystallographica*, Volume B25, pages 925 to 945 (1969), the ionic radii of high spin Cr³⁺, low spin Co³⁺, low spin Ni³⁺, high spin Ni³⁺, and Ni²⁺ are 62 pm, 53 pm, 56 pm, 60 pm, and 69 pm, respectively. As discussed in co-pending U. S. Patent Application CL-2099, substitution of Co³⁺ for Cr³⁺
 15 in the α -Cr₂O₃ lattice results in a slight contraction of the unit cell. In the case of the present invention where nickel or both nickel and cobalt are substituted into the α -Cr₂O₃ lattice, the unit cell may expand or contract depending on the oxidation state and spin state of nickel and whether cobalt is present or not.

20

TABLE 3

Characterization of Metal-Substituted alpha-Chromium(III) Oxides

25	Cr/Co/Ni	Lattice parameters		Unit Cell
	Composition			
	<u>atom %</u>	<u>a, nm</u>	<u>c, nm</u>	<u>Volume (nm³)</u>
	Cr100%	0.49321	1.35207	0.284839
	Cr95%/Co3%/Ni2%	0.49292	1.35127	0.284332
	Cr98%/Ni2%	0.49378	1.35327	0.285743
30	Cr95%/Ni5%	0.49371	1.35358	0.285743

a. Estimated in error in a, c, and unit cell volume are 0.00001 nm, 0.00002 nm, and 0.000013 nm³, respectively.

Results for cobalt-substituted alpha-chromium oxide compositions
 35 disclosed in co-pending U.S. Patent Application No. 60/405,220 [CL2099 US PRV], filed August 22, 2002, indicate the solubility limit for cobalt in the α -Cr₂O₃ phase is about 6 atom %. XAS and XRD data for the nickel-substituted alpha-chromium oxide compositions nominally containing 2%

nickel and 5% nickel indicate that the solubility limit for nickel in the α - Cr_2O_3 lattice is about 2 atom % (see Preparation Examples 7 and 8).

Other phases such as chromium-nickel and chromium-cobalt spinel phases may be present in the chromium oxide compositions of the present invention particularly at higher loadings of cobalt or nickel. The presence of these phases is detected by EDS, TEM, and XAS.

The surface area of the chromium oxide compositions of the present invention is typically in the range of about 1 to 100 m²/gram. The α - $\text{Ni}_x\text{Co}_y\text{Cr}_{2-x-y}\text{O}_3$ phase present in the compositions prepared by the process of this invention is typically made up of crystallites having particle sizes varying from about 20 to about 400 nm, typically from about 40 to about 250 nm. Included in this invention are microcrystalline materials with particle sizes smaller than 20 nm.

The calcined chromium oxide compositions of the present invention may be formed into various shapes such as pellets, granules, and extrudates for use in packing reactors. They may also be used in powder form.

The compositions of this invention may further comprise one or more additives in the form of metal compounds that alter the selectivity or activity of the crystalline nickel-substituted or crystalline mixed nickel- and cobalt-substituted alpha-chromium oxides or the fluorinated substituted alpha-chromium oxides. Suitable additives may be selected from the group consisting of fluorides, oxides, or oxyfluoride compounds of Mg, Ca, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Ce, and Zn.

The total content of the additive(s) in the compositions of the present invention may be from about 0.05 atom % to about 15 atom % based on the total metal content of the compositions. The additives may be incorporated into the compositions of the present invention by standard procedures such as by impregnation.

Typically, the calcined compositions will be pre-treated with a fluorinating agent prior to use as catalysts for changing the fluorine content of halogenated hydrocarbon compounds. Typically this fluorinating agent is HF though other materials may be used such sulfur tetrafluoride, carbonyl fluoride, and fluorinated hydrocarbon compounds such as trichlorofluoromethane, dichlorodifluoromethane, chlorodifluoromethane, trifluoromethane, or 1,1,2-trichlorotrifluoroethane. This pretreatment can be accomplished, for example, by placing the catalyst in a suitable

container which can be the reactor to be used to perform the process in the instant invention, and thereafter, passing HF over the dried, calcined catalyst so as to partially saturate the catalyst with HF. This is conveniently carried out by passing HF over the catalyst for a period of
5 time, for example, about 0.1 to about 10 hours at a temperature of, for example, about 200°C to about 450°C. Nevertheless, this pre-treatment is not essential.

As noted above, catalysts provided in accordance with this invention may be used to change the fluorine distribution in hydrocarbons
10 and/or halogenated hydrocarbons. The fluorine distribution in a hydrocarbon or a halogenated hydrocarbon may be changed by increasing the fluorine content of the hydrocarbon or halogenated hydrocarbon. The fluorine distribution of a halogenated hydrocarbon may also be changed by decreasing the fluorine content of the halogenated hydrocarbon, and/or
15 rearranging the placement of fluorine atoms on the carbon atoms of the halogenated hydrocarbon. Of note are processes where the fluorine distribution in halogenated hydrocarbons containing from one to twelve carbon atoms is changed, particularly processes where the fluorine distribution in halogenated hydrocarbons containing one to six carbon
20 atoms is changed. Also of note are processes where the fluorine content of hydrocarbons containing from one to twelve carbon atoms is increased, particularly processes where the fluorine content in hydrocarbons containing one to six carbon atoms is increased. Processes for changing the fluorine distribution in halogenated hydrocarbons include fluorination,
25 chlorofluorination, isomerization, disproportionation, dehydrofluorination, and chlorodefluorination. Processes for increasing the fluorine content of hydrocarbons include fluorination and chlorofluorination. The processes of this invention are characterized by using as the catalyst a composition comprising at least one chromium-containing component selected from the
30 group consisting of the crystalline nickel-substituted alpha-chromium oxide, crystalline mixed nickel- and cobalt-substituted alpha- chromium oxide as described above, and said substituted alpha-chromium oxide which has been treated with a fluorinating agent. Typical of saturated halogenated hydrocarbons suitable for fluorination, chlorofluorination,
35 isomerization, disproportionation, dehydrofluorination, and chlorodefluorination processes are those which have the formula $C_nH_aBr_bCl_cF_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, and d is an

integer from 0 to 13, the sum of b, c, and d is at least 1, and that the sum of a, b, c, and d is equal to $2n + 2$, provided that n is at least 2 for isomerization, disproportionation, and dehydrofluorination processes, a is at least one for dehydrofluorination processes, b is 0 for

5 chlorodefluorination processes, b + c is at least 1 for fluorination processes and is 0 for dehydrofluorination processes, a + b + c is at least 1 for fluorination, chlorodefluorination, isomerization, disproportionation, and dehydrofluorination processes, and d is at least 1 for isomerization, disproportionation, dehydrofluorination, and chlorodefluorination

10 processes. Typical of unsaturated halogenated hydrocarbons suitable for fluorination, chlorofluorination, isomerization, disproportionation, and chlorodefluorination processes are those which have the formula $C_pH_eBr_fCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, and h is an

15 integer from 0 to 11, the sum of f, g, and h is at least 1, and that the sum of e, f, g, and h is equal to $2p$, provided that f is 0 for chlorodefluorination processes, e + f + g is at least 1 for isomerization and disproportionation processes, and h is at least 1 for isomerization, disproportionation, and chlorodefluorination processes. Typical of saturated hydrocarbons

20 suitable for chlorofluorination are those which have the formula C_qH_r where q is an integer from 1 to 6 and r is $2q + 2$. Typical of unsaturated hydrocarbons suitable for fluorination and chlorofluorination are those which have the formula C_iH_j where i is an integer from 2 to 6 and j is $2i$.

Fluorination

25 Included in this invention is a process for increasing the fluorine content of a halogenated hydrocarbon or an unsaturated hydrocarbon compound by reacting said compound(s) with hydrogen fluoride in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of

30 the crystalline nickel-substituted alpha-chromium oxide or crystalline mixed nickel- and cobalt-substituted alpha-chromium oxide described above, and said substituted alpha-chromium oxide which has been treated with a fluorinating agent. The catalyst composition may optionally contain additional components such as additives to alter the activity and selectivity

35 of the catalyst.

Halogenated hydrocarbon compounds suitable as starting materials for the fluorination process of this invention may be saturated or unsaturated. Saturated halogenated hydrocarbon compounds suitable for

the fluorination process of this invention include those of the general formula $C_nH_aBr_bCl_cF_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, and d is an integer from 0 to 13, and the sum of a, b, c, and d is equal to $2n + 2$,
5 provided that b or c is at least 1. Unsaturated halogenated hydrocarbon compounds suitable for the process of this invention are given by the general formula $C_pH_eBr_fCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, and h is an integer from 0 to 11, the sum of f, g, and h is at least 1 and
10 the sum of e, f, g, and h is equal to $2p$. Unsaturated hydrocarbons suitable for fluorination are those which have the formula C_iH_j where i is an integer from 2 to 6 and j is $2i$. The fluorine content of saturated compounds of the formula $C_nH_aBr_bCl_cF_d$, unsaturated compounds of the formula $C_pH_eBr_fCl_gF_h$ and/or unsaturated compounds of the formula C_iH_j may be
15 increased by reacting said compounds with HF in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline nickel-substituted alpha-chromium oxide described above, the crystalline mixed nickel- and cobalt-substituted alpha-chromium oxide described
20 above, and said substituted alpha-chromium oxide which has been treated with a fluorinating agent. Such a process is referred to herein as a vapor phase fluorination reaction.

The vapor phase fluorination reactions are typically conducted at temperatures of from about 150°C to 500°C. For saturated compounds
25 the fluorination is preferably carried out from about 175°C to 400°C and more preferably from about 200°C to about 350°C. For unsaturated compounds the fluorination is preferably carried out from about 150°C to 350°C and more preferably from about 175°C to about 300°C.

The vapor phase fluorination reactions are typically conducted at
30 atmospheric and superatmospheric pressures. For reasons of convenience in downstream separations processes (e.g., distillation), pressures of up to about 30 atmospheres may be employed.

The vapor phase fluorination reactions are typically conducted in a tubular reactor. The reactor and its associated feed lines, effluent lines,
35 and associated units should be constructed of materials resistant to hydrogen fluoride and hydrogen chloride. Typical materials of construction, well-known to the fluorination art, include stainless steels, in particular of the austenitic type, the well-known high nickel alloys, such as

Monel® nickel-copper alloys, Hastelloy® nickel-based alloys and, Inconel® nickel-chromium alloys, and copper-clad steel.

The contact time in the reactor is typically from about 1 to about 120 seconds and preferably from about 5 to about 60 seconds.

- 5 The amount of HF reacted with the unsaturated hydrocarbons or halogenated hydrocarbon compounds should be at least a stoichiometric amount. The stoichiometric amount is based on the number of Br and/or Cl substituents to be replaced by F in addition to one mole of HF to saturate the carbon-carbon double bond if present. Typically, the molar
- 10 ratio of HF to the said compounds of the formulas $C_nH_aBr_bCl_cF_d$, $C_pH_eBr_fCl_gF_h$, and C_iH_j can range from about 0.5:1 to about 100:1, preferably from about 2:1 to about 50:1, and more preferably from about 3:1 to about 20:1. In general, with a given catalyst composition, the higher the temperature and the longer the contact time, the greater is the
- 15 conversion to fluorinated products. The above variables can be balanced, one against the other, so that the formation of higher fluorine substituted products is maximized.

- Examples of saturated compounds of the formula $C_nH_aBr_bCl_cF_d$ which may be reacted with HF in the presence of the catalyst of this
- 20 invention include CH_2Cl_2 , CH_2Br_2 , $CHCl_3$, CCl_4 , C_2Cl_6 , C_2BrCl_5 , C_2Cl_5F , $C_2Cl_4F_2$, $C_2Cl_3F_3$, $C_2Cl_2F_4$, C_2ClF_5 , C_2HCl_5 , C_2HCl_4F , $C_2HCl_3F_2$, $C_2HCl_2F_3$, C_2HClF_4 , C_2HBrF_4 , $C_2H_2Cl_4$, $C_2H_2Cl_3F$, $C_2H_2Cl_2F_2$, $C_2H_2ClF_3$, $C_2H_3Cl_3$, $C_2H_3Cl_2F$, $C_2H_3ClF_2$, $C_2H_4Cl_2$, C_2H_4ClF , $C_3Cl_6F_2$, $C_3Cl_5F_3$, $C_3Cl_4F_4$, $C_3Cl_3F_5$, C_3HCl_7 , C_3HCl_6F , $C_3HCl_5F_2$, $C_3HCl_4F_3$,
- 25 $C_3HCl_3F_4$, $C_3HCl_2F_5$, $C_3H_2Cl_6$, $C_3H_2BrCl_5$, $C_3H_2Cl_5F$, $C_3H_2Cl_4F_2$, $C_3H_2Cl_3F_3$, $C_3H_2Cl_2F_4$, $C_3H_2ClF_5$, $C_3H_3Cl_5$, $C_3H_3Cl_4F$, $C_3H_3Cl_3F_2$, $C_3H_3Cl_2F_3$, $C_3H_3ClF_4$, $C_3H_4Cl_4$, $C_4Cl_4Cl_4$, $C_4Cl_4Cl_6$, $C_4H_5Cl_5$, $C_4H_5Cl_4F$, and $C_5H_4Cl_8$.

- Specific examples of fluorination reactions of saturated halogenated
- 30 hydrocarbon compounds which may be carried out under the conditions described above using the catalysts of this invention include the conversion of CH_2Cl_2 to CH_2F_2 , the conversion of $CHCl_3$ to a mixture of $CHCl_2F$, $CHClF_2$, and CHF_3 , the conversion of CH_3CHCl_2 to a mixture of CH_3CHClF and CH_3CHF_2 , the conversion of CH_2ClCH_2Cl to a mixture of
- 35 CH_3CHClF and CH_3CHF_2 , the conversion of CH_3CCl_3 to a mixture of CH_3CCl_2F , CH_3CClF_2 , and CH_3CF_3 , the conversion of CH_2ClCF_3 to CH_2FCF_3 , the conversion of $CHCl_2CF_3$ to a mixture of $CHClFCF_3$ and CHF_2CF_3 , the conversion of $CHClFCF_3$ to CHF_2CF_3 , the conversion of

- CHBrFCF₃ to CHF₂CF₃, the conversion of CCl₃CF₂CCl₃ to a mixture of CCl₂FCF₂CClF₂ and CClF₂CF₂CClF₂, the conversion of CCl₃CH₂CCl₃ to CF₃CH₂CF₃, the conversion of CCl₃CH₂CHCl₂ to a mixture of CF₃CH₂CHF₂, CF₃CH=CHCl, and CF₃CH=CHF, the conversion of
- 5 CF₃CCl₂CClF₂ to a mixture of CF₃CCl₂CF₃, and CF₃ClFCF₃, the conversion of CF₃CCl₂CF₃ to CF₃ClFCF₃, and the conversion of a mixture comprising CF₃CF₂CHCl₂ and CClF₂CF₂CHClF to a mixture of CF₃CF₂CHClF and CF₃CF₂CHF₂.

- Examples of unsaturated compounds of the formula C_pH_eBr_fCl_gF_h and C_iH_j which may be reacted with HF in the presence of the catalysts of this invention include C₂Cl₄, C₂BrCl₃, C₂Cl₃F, C₂Cl₂F₂, C₂ClF₃, C₂F₄, C₂HCl₃, C₂HBrCl₂, C₂HCl₂F, C₂HClF₂, C₂HF₃, C₂H₂Cl₂, C₂H₂ClF, C₂H₂F₂, C₂H₃Cl, C₂H₃F, C₂H₄, C₃H₆, C₃H₅Cl, C₃H₄Cl₂, C₃H₃Cl₃, C₃H₂Cl₄, C₃HCl₅, C₃Cl₆, C₃Cl₅F, C₃Cl₄F₂, C₃Cl₃F₃, C₃Cl₂F₄, C₃ClF₅, C₃HF₅, C₃H₂F₄, C₃F₆, C₄Cl₈, C₄Cl₂F₆, C₄ClF₇, C₄H₂F₆, and C₄HClF₆.
- 15

- Specific examples of fluorination reactions of unsaturated halogenated hydrocarbon compounds which may be carried out using the catalysts of this invention include the conversion of CHCl=CCl₂ to a mixture of CH₂ClCF₃ and CH₂FCF₃, the conversion of CCl₂=CCl₂ to a mixture of CHCl₂CF₃, CHClFCF₃, and CHF₂CF₃, the conversion of CCl₂=CH₂ to a mixture of CH₃CCl₂F, CH₃CClF₂, and CH₃CF₃, the conversion of CH₂=CHCl to a mixture of CH₃CHClF and CH₃CHF₂, the conversion of CF₂=CH₂ to CH₃CF₃, the conversion of CCl₂=CClCF₃ to a mixture of CF₃CHClCClF₂, CF₃CHClCF₃, and/or CF₃CCl=CF₂, the
- 20
- conversion of CF₃CF=CF₂ to CF₃CHFCF₃, the conversion of CF₃CH=CF₂ to CF₃CH₂CF₃, and the conversion of CF₃CH=CHF to CF₃CH₂CHF₂.
- 25

- Mixtures of saturated halogenated hydrocarbon compounds or mixtures of unsaturated hydrocarbons and/or halogenated hydrocarbon compounds may also be used in the vapor phase fluorination reactions as well as mixtures comprising both unsaturated hydrocarbons and halogenated hydrocarbon compounds. Specific examples of mixtures of saturated halogenated hydrocarbon compounds and mixtures of unsaturated hydrocarbons and unsaturated halogenated hydrocarbon compounds that may be subjected to vapor phase fluorination using the catalysts of this invention include a mixture of CH₂Cl₂ and CCl₂=CCl₂, a mixture of CCl₂FCClF₂ and CCl₃CF₃, a mixture of CCl₂=CCl₂ and CCl₂=CClCCl₃, a mixture of CH₂=CHCH₃ and CH₂=CClCH₃, a mixture of CH₂Cl₂ and CH₃CCl₃, a mixture of CHF₂CClF₂ and CHClFCF₃, a mixture
- 30
- 35

- of $\text{CHCl}_2\text{CCl}_2\text{CH}_2\text{Cl}$ and $\text{CCl}_3\text{CHClCH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CH}_2\text{CCl}_3$ and $\text{CCl}_3\text{CHClCH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CHClCCl}_3$, $\text{CCl}_3\text{CH}_2\text{CCl}_3$, and $\text{CCl}_3\text{CCl}_2\text{CH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CH}_2\text{CCl}_3$ and $\text{CCl}_3\text{CH}_2\text{CCl}_3$, a mixture of and $\text{CF}_3\text{CH}_2\text{CCl}_2\text{F}$ and $\text{CF}_3\text{CH}=\text{CCl}_2$, and a mixture of
- 5 $\text{CF}_3\text{CH}=\text{CHCl}$ and $\text{CF}_3\text{CH}=\text{CCl}_2$.

Chlorofluorination

- Included in this invention is a process for increasing the fluorine content of a hydrocarbon compound or a halogenated hydrocarbon compound by reacting said compound with hydrogen fluoride (HF) and
- 10 chlorine (Cl_2) in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline nickel-substituted alpha- chromium oxide described above, the crystalline mixed nickel- and cobalt-substituted alpha-chromium oxide described above, and said substituted alpha-
- 15 chromium oxide which has been treated with a fluorinating agent. The catalyst composition may optionally contain additional components such as another catalytically effective metal.

- Halogenated hydrocarbon compounds suitable as starting materials for the chlorofluorination process of this invention may be saturated or
- 20 unsaturated. Saturated halogenated hydrocarbon compounds suitable for the fluorination process of this invention include those of the general formula $\text{C}_n\text{H}_a\text{Br}_b\text{Cl}_c\text{F}_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, and d is an integer from 0 to 13, the sum of b, c, and d is at least 1, and the sum
- 25 of a, b, c, and d is equal to $2n + 2$, provided that $a + b + c$ is at least 1. Preferred chlorofluorination processes include those involving said saturated starting materials where a is at least 1. Saturated hydrocarbon compounds suitable for chlorofluorination are those which have the formula C_qH_r where q is an integer from 1 to 6 and r is $2q + 2$.
- 30 Unsaturated halogenated hydrocarbon compounds suitable for the chlorofluorination processes of this invention include those of the general formula $\text{C}_p\text{H}_e\text{Br}_f\text{Cl}_g\text{F}_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, and h is an integer from 0 to 11, the sum of f, g, and h is at least 1 and the sum
- 35 of e, f, g, and h is equal to $2p$. Unsaturated hydrocarbon compounds suitable for fluorination are those which have the formula C_iH_j where i is an integer from 2 to 6 and j is $2i$. The fluorine content of saturated compounds of the formulas $\text{C}_n\text{H}_a\text{Br}_b\text{Cl}_c\text{F}_d$ and C_qH_r and/or unsaturated

compounds of the formulas $C_pH_eBr_fCl_gF_h$ and C_iH_j may be increased by reacting said compounds with HF and Cl_2 in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline
 5 nickel-substituted alpha-chromium oxide described above, the crystalline mixed nickel- and cobalt-substituted alpha-chromium oxide described above, and said substituted alpha-chromium oxide which has been treated with a fluorinating agent. Such a process is referred to herein as a vapor phase chlorofluorination reaction.

10 The conditions of the vapor phase chlorofluorination reactions are similar to those described above for vapor phase fluorination reactions in terms of the temperature ranges, contact times, pressures, and mole ratios of HF to the halogenated hydrocarbon compounds. The amount of chlorine (Cl_2) fed to the reactor is based on whether the halogenated hydrocarbon
 15 compounds fed to the reactor is unsaturated and the number of hydrogens in $C_nH_aBr_bCl_cF_d$, C_qH_r , $C_pH_eBr_fCl_gF_h$, and C_iH_j that are to be replaced by chlorine and fluorine. One mole of Cl_2 is required to saturate a carbon-carbon double bond and a mole of Cl_2 is required for every hydrogen to be replaced by chlorine or fluorine. A slight excess of chlorine over the
 20 stoichiometric amount may be necessary for practical reasons, but large excesses of chlorine will result in complete chlorofluorination of the products. The ratio of Cl_2 to halogenated hydrocarbon compound is typically from about 1:1 to about 10:1.

Specific examples of vapor phase chlorofluorination reactions of
 25 saturated halogenated hydrocarbon compounds of the general formula $C_nH_aBr_bCl_cF_d$ and saturated hydrocarbon compounds of the general formula C_qH_r which may be carried out using the catalysts of this invention include the conversion of C_2H_6 to a mixture containing CH_2ClCF_3 , the conversion of CH_2ClCF_3 to a mixture of $CHClCF_3$ and CHF_2CF_3 , the
 30 conversion of $CCl_3CH_2CH_2Cl$ to a mixture of $CF_3CCl_2CClF_2$, $CF_3CCl_2CF_3$, $CF_3CClFCClF_2$, and $CF_3CClFCF_3$, the conversion of $CCl_3CH_2CHCl_2$ to a mixture of $CF_3CCl_2CClF_2$, $CF_3CCl_2CF_3$, $CF_3CClFCClF_2$, and $CF_3CClFCF_3$, the conversion of $CCl_3CHClCH_2Cl$ to a mixture of $CF_3CCl_2CClF_2$, $CF_3CCl_2CF_3$, $CF_3CClFCClF_2$, and
 35 $CF_3CClFCF_3$, the conversion of $CHCl_2CCl_2CH_2Cl$ to a mixture of $CF_3CCl_2CClF_2$, $CF_3CCl_2CF_3$, $CF_3CClFCClF_2$, and $CF_3CClFCF_3$, the conversion of $CCl_3CH_2CH_2Cl$ to a mixture of $CF_3CCl_2CHF_2$, $CF_3CClFCHF_2$, $CF_3CClFCClF_2$, and $CF_3CCl_2CF_3$, and the conversion of

$\text{CCl}_3\text{CH}_2\text{CHCl}_2$ to a mixture of $\text{CF}_3\text{CCl}_2\text{CHF}_2$, $\text{CF}_3\text{CClFCHF}_2$, $\text{CF}_3\text{CClFCClF}_2$, and $\text{CF}_3\text{CCl}_2\text{CF}_3$.

Specific examples of vapor phase chlorofluorination reactions of unsaturated halogenated hydrocarbon compounds of the general formula $\text{C}_p\text{H}_e\text{Br}_f\text{Cl}_g\text{F}_h$ and unsaturated hydrocarbon compounds of the general formula C_iH_j which may be carried out using the catalysts of this invention include the conversion of C_2H_4 to a mixture of $\text{CCl}_3\text{CClF}_2$, $\text{CCl}_2\text{FCCl}_2\text{F}$, $\text{CClF}_2\text{CCl}_2\text{F}$, CCl_3CF_3 , $\text{CF}_3\text{CCl}_2\text{F}$, and $\text{CClF}_2\text{CClF}_2$, the conversion of C_2Cl_4 to a mixture of $\text{CCl}_3\text{CClF}_2$, $\text{CCl}_2\text{FCCl}_2\text{F}$, $\text{CClF}_2\text{CCl}_2\text{F}$, CCl_3CF_3 , $\text{CF}_3\text{CCl}_2\text{F}$, and $\text{CClF}_2\text{CClF}_2$, and the conversion of C_3H_6 or $\text{CF}_3\text{CCl}=\text{CCl}_2$ to a mixture of $\text{CF}_3\text{CCl}_2\text{CClF}_2$, $\text{CF}_3\text{CCl}_2\text{CF}_3$, $\text{CF}_3\text{CClFCClF}_2$, and $\text{CF}_3\text{CClFCF}_3$.

Of note is a catalytic process for producing a mixture of 1,2,2-trichloro-1,1,3,3,3-pentafluoropropane (i.e., $\text{CClF}_2\text{CCl}_2\text{CF}_3$ or CFC-215aa), 2,2-dichloro-1,1,1,3,3,3-hexafluoropropane (i.e., $\text{CF}_3\text{CCl}_2\text{CF}_3$ or CFC-216aa), 1,2-dichloro-1,1,1,3,3,3-hexafluoropropane (i.e., $\text{CClF}_2\text{CClFCF}_3$ or CFC-216ba), and 2-chloro-1,1,1,2,3,3,3-heptafluoropropane (i.e., $\text{CF}_3\text{CClFCF}_3$ or CFC-217ba), by the chlorofluorination of a hexahalopropene of the formula $\text{C}_3\text{Cl}_{6-x}\text{F}_x$, wherein x equals 0 to 4. Preferred hexahalopropenes of the formula $\text{C}_3\text{Cl}_{6-x}\text{F}_x$ include 1,2,2-trichloro-3,3,3-trifluoro-1-propene (i.e., $\text{CCl}_2=\text{CClCF}_3$ or CFC-1213xa) and hexachloropropene (i.e., $\text{CCl}_2=\text{CClCCl}_3$). The mixture of CFC-215aa, -216aa, -216ba, and -217ba is produced by reacting the above unsaturated compounds with Cl_2 and HF in the vapor phase in the presence of the catalysts of this invention at temperatures from about 150°C to about 450°C , preferably about 250°C to 400°C .

The amount of HF fed to the reactor should be at least a stoichiometric amount based on the number of Cl substituents in the $\text{C}_3\text{Cl}_{6-x}\text{F}_x$ starting material(s) and the desired composition of the final product. In the case of chlorofluorination of CFC-1213xa to a mixture of chlorofluoropropanes having an average number of fluorine substituents of six, the stoichiometric ratio of HF to CFC-1213xa is 3:1. Preferred ratios of HF to $\text{C}_3\text{Cl}_{6-x}\text{F}_x$ starting material(s) are typically in the range of about the stoichiometric ratio to about 30:1, more preferably from about 8:1 to 25:1.

The amount of chlorine fed to the reactor should be at least a stoichiometric amount. Preferred molar ratios of Cl_2 to CFC-1213xa are from about 1:1 to about 5:1.

Preferred contact times are from about 5 seconds to about 60 seconds.

Further information on the chlorofluorination of CFC-1213xa is provided in U.S. Patent Application 60/405,222 [CL2108 US PRV] filed August 22, 2002, and hereby incorporated by reference herein in its entirety.

Mixtures of saturated hydrocarbon compounds and saturated halogenated hydrocarbon compounds and mixtures of unsaturated hydrocarbon compounds and unsaturated halogenated hydrocarbon compounds as well as mixtures comprising both saturated and unsaturated compounds may be chlorofluorinated using the catalysts of the present invention. Specific examples of mixtures of saturated and unsaturated hydrocarbons and halogenated hydrocarbons that may be used include a mixture of $\text{CCl}_2=\text{CCl}_2$ and $\text{CCl}_2=\text{CClCCl}_3$, a mixture of $\text{CHCl}_2\text{CCl}_2\text{CH}_2\text{Cl}$ and $\text{CCl}_3\text{CHClCH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CH}_2\text{CCl}_3$ and $\text{CCl}_3\text{CHClCH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CHClCCl}_3$, $\text{CCl}_3\text{CH}_2\text{CCl}_3$, and $\text{CCl}_3\text{CCl}_2\text{CH}_2\text{Cl}$, a mixture of $\text{CHF}_2\text{CH}_2\text{CF}_3$ and $\text{CHCl}=\text{CHCF}_3$, and a mixture of $\text{CH}_2=\text{CH}_2$ and $\text{CH}_2=\text{CHCH}_3$.

Isomerization and Disproportionation

Included in this invention is a process for changing the fluorine distribution in a halogenated hydrocarbon compound by isomerizing said halogenated hydrocarbon compound in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline nickel-substituted alpha-chromium oxide described above, the mixed nickel- and cobalt-substituted alpha-chromium oxide described above, and said substituted alpha-chromium oxide which has been treated with a fluorinating agent.

Also included in this invention is a process for changing the fluorine distribution in a halogenated hydrocarbon compound by disproportionating said halogenated hydrocarbon compound in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline nickel-substituted alpha-chromium oxide described above, the nickel- and cobalt-substituted alpha-chromium oxide described above, and said nickel-substituted (and optionally cobalt-substituted) alpha-chromium oxide which has been treated with a fluorinating agent.

Halogenated hydrocarbon compounds suitable as starting materials for the isomerization and disproportionation processes of this invention

may be saturated or unsaturated. Saturated halogenated hydrocarbon compounds suitable for the isomerization and disproportionation processes of this invention include those of the general formula $C_nH_aBr_bCl_cF_d$, wherein n is an integer from 2 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, and d is an integer from 1 to 13, and the sum of a, b, c, and d is equal to $2n + 2$, provided that $a + b + c$ is at least 1. Unsaturated halogenated hydrocarbon compounds suitable for the isomerization and disproportionation processes of this invention include those of the general formula $C_pH_eBr_fCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, and h is an integer from 1 to 11, and the sum of e, f, g, and h is equal to $2p$, provided that the sum of e, f, and g is at least 1.

In one embodiment of the present invention, the fluorine distribution of a halogenated hydrocarbon compound is changed by rearranging the H, Br, and/or Cl substituents in the molecule (typically to a thermodynamically preferred arrangement) while maintaining the same number of H, Br, Cl, and F substituents, respectively. This process is referred to herein as isomerization.

In another embodiment of the present invention, the fluorine distribution of a halogenated hydrocarbon compound is changed by exchanging at least one F substituent of one molecule of the halogenated hydrocarbon starting material with at least one H, Br, and/or Cl substituent of another molecule of the halogenated hydrocarbon starting material so as to result in the formation of one or more halogenated hydrocarbon compounds having a decreased fluorine content compared to the halogenated hydrocarbon starting material and one or more halogenated hydrocarbon compounds having an increased fluorine content compared to the halogenated hydrocarbon starting material. This process is referred to herein as disproportionation.

In another embodiment of the present invention, said contacting of halogenated hydrocarbon compounds can result in the formation of one or more pairs of halogenated hydrocarbon compounds. In this case, one member of the pair has a larger number of H, Br, Cl, or F substituents and the other member of the pair has a lower number of H, Br, Cl, or F substituents. This process is referred to herein as disproportionation.

In another embodiment of the present invention, both isomerization and disproportionation reactions may occur simultaneously.

Whether carrying out isomerization, disproportionation, or both isomerization and disproportionation, the fluorine distribution of saturated compounds of the formula $C_nH_aBr_bCl_cF_d$ and/or unsaturated compounds of the formula $C_pH_eBr_fCl_gF_h$ may be changed in the presence of a catalyst

5 composition comprising at least one chromium-containing component selected from the group consisting of the crystalline nickel-substituted alpha-chromium oxide described above, the mixed nickel- and cobalt-substituted alpha-chromium oxide described above, and said substituted alpha-chromium oxide which has been treated with a fluorinating agent.

10 The isomerization and disproportionation reactions are typically conducted at temperatures of from about 150°C to 500°C, preferably from about 200°C to about 400°C. The contact time in the reactor is typically from about 1 to about 120 seconds and preferably from about 5 to about 60 seconds. The isomerization and disproportionation reactions may be

15 carried out in the presence of an inert gas such as helium, argon, or nitrogen though this is not preferred. The isomerization and disproportionation reactions may be carried out in the presence of small amounts of HF and HCl, but this is not preferred.

Specific examples of vapor phase isomerization reactions which

20 may be carried out using the catalysts of this invention include the conversion of $CClF_2CCl_2F$ to CCl_3CF_3 , the conversion of $CClF_2CClF_2$ to CF_3CCl_2F , the conversion of CHF_2CClF_2 to CF_3CHClF , the conversion of CHF_2CHF_2 to CF_3CH_2F , the conversion of $CF_3CClFCClF_2$ to $CF_3CCl_2CF_3$, and the conversion of $CF_3CHFCHF_2$ to $CF_3CH_2CF_3$.

25 Specific examples of vapor phase disproportionation reactions which may be carried out using the catalysts of this invention include the conversion of $CClF_2CClF_2$ to a mixture of $CClF_2CCl_2F$, CCl_3CF_3 , and CF_3CClF_2 and the conversion of $CHClFCF_3$ to a mixture of $CHCl_2CF_3$, and CHF_2CF_3 .

30 Of note is a process for the conversion of a mixture of 2-chloro-1,1,2,2-tetrafluoroethane (i.e., CHF_2CClF_2 or HCFC-124a) and 2-chloro-1,1,1,2-tetrafluoroethane (i.e., CF_3CHClF or HCFC-124) to a mixture comprising 2,2-dichloro-1,1,1-trifluoroethane (i.e., $CHCl_2CF_3$ or HCFC-123) and 1,1,1,2,2-pentafluoroethane (i.e., CF_3CHF_2 or HFC-125) in

35 addition to unconverted starting materials. The mixture comprising HFC-125 and HCFC-123 may be obtained in the vapor phase by contacting a mixture of HCFC-124a and -124 over the catalysts of this invention optionally in the presence of a diluent selected from the group consisting

of HF, HCl, nitrogen, helium, argon, and carbon dioxide. The disproportionation is preferably conducted at about 150°C to about 400°C, more preferably about 250°C to about 350°C. If used, the diluent gas, may be present in a molar ratio of diluent to haloethane of from about 1:1
5 to about 5:1. Preferred contact times are from about 10 seconds to about 60 seconds.

Dehydrofluorination

Included in this invention is a process for decreasing the fluorine content of a halogenated hydrocarbon compound by dehydrofluorinating
10 said halogenated hydrocarbon compound in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline nickel-substituted alpha-chromium oxide described above, the mixed nickel- and cobalt-substituted alpha-chromium oxide described above, and said substituted
15 alpha-chromium oxide which has been treated with a fluorinating agent.

Halogenated hydrocarbon compounds suitable as starting materials for the dehydrofluorination process of this invention are typically saturated. Saturated halogenated hydrocarbon compounds suitable for the dehydrofluorination process of this invention include those of the general
20 formula $C_nH_aF_d$, wherein n is an integer from 2 to 6, a is an integer from 1 to 12, d is an integer from 1 to 13, and the sum of a and d is equal to $2n + 2$. The fluorine content of saturated compounds of the formula $C_nH_aF_d$ may be decreased in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group
25 consisting of the crystalline nickel-substituted alpha-chromium oxide described above, the mixed nickel- and cobalt-substituted alpha-chromium oxide described above, and said substituted alpha-chromium oxide which has been treated with a fluorinating agent. This decrease in fluorine content is typically associated with removal of hydrogen fluoride (HF) from
30 the molecule and is referred to herein as dehydrofluorination.

The dehydrofluorination reactions are typically conducted at temperatures of from about 200°C to about 500°C, preferably from about 300°C to about 450°C. The contact time in the reactor is typically from about 1 to about 360 seconds and preferably from about 5 to about
35 120 seconds. Carrying out the dehydrofluorination reactions in the presence of an inert gas such as helium, argon, or nitrogen promotes the dissociation of the fluorinated hydrocarbon compound, but this practice can also lead to difficulties in separation and is not preferred.

The product of dehydrofluorination reaction consists of HF and the unsaturated fluorinated hydrocarbon compound resulting from loss of HF from the starting material. Specific examples of vapor phase dehydrofluorination reactions which may be carried out using the catalysts of this invention include the conversion of CH_3CHF_2 to $\text{CH}_2=\text{CHF}$, the conversion of CH_3CF_3 to $\text{CH}_2=\text{CF}_2$, the conversion of $\text{CF}_3\text{CH}_2\text{F}$ to $\text{CF}_2=\text{CHF}$, the conversion of $\text{CHF}_2\text{CH}_2\text{CF}_3$ to $\text{CHF}=\text{CHCF}_3$, and the conversion of $\text{CF}_3\text{CH}_2\text{CF}_3$ to $\text{CF}_3\text{CH}=\text{CF}_2$.

Of note is a catalytic process for producing fluoroethene (i.e., $\text{CH}_2=\text{CHF}$ or vinyl fluoride) by the dehydrofluorination of a 1,1-difluoroethane (i.e., CHF_2CH_3 or HFC-152a). A mixture comprising vinyl fluoride and unconverted HFC-152a may be obtained in the vapor phase by contacting HFC-152a over the catalysts of this invention optionally in the presence of a diluent selected from the group consisting of HF, nitrogen, helium, argon, and carbon dioxide. The dehydrofluorination is preferably conducted at about 150°C to about 400°C , more preferably about 250°C to about 350°C . If used, the diluent gas, may be present in a molar ratio of diluent to haloethane of from about 1:1 to about 5:1. Preferred contact times are from about 10 seconds to about 60 seconds.

Chlorodefluorination

Included in this invention is a process for decreasing the fluorine content of a halogenated hydrocarbon compound by reacting said halogenated hydrocarbon compound with hydrogen chloride (HCl) in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline nickel-substituted alpha-chromium oxide described above, the mixed nickel- and cobalt-substituted alpha-chromium oxide described above, and said substituted alpha-chromium oxide which has been treated with a fluorinating agent.

Halogenated hydrocarbon compounds suitable as starting materials for the chlorodefluorination process of this invention may be saturated or unsaturated. Saturated halogenated hydrocarbon compounds suitable for the chlorodefluorination processes of this invention include those of the general formula $\text{C}_n\text{H}_a\text{Cl}_c\text{F}_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, c is an integer from 0 to 13, and d is an integer from 1 to 13, and the sum of a, c, and d is equal to $2n + 2$. Unsaturated halogenated hydrocarbon compounds suitable for the chlorodefluorination process of this invention include those of the general formula $\text{C}_p\text{H}_e\text{Cl}_g\text{F}_h$,

wherein p is an integer from 2 to 6, e is an integer from 0 to 10, g is an integer from 0 to 12, h is an integer from 1 to 11, and the sum of e, g, and h is equal to 2p. The fluorine content of saturated compounds of the formula $C_nH_aCl_eF_d$ and unsaturated compounds of the formula $C_pH_eCl_gF_h$ may be decreased by reacting said compounds in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline nickel-substituted alpha-chromium oxide described above, the mixed nickel- and cobalt-substituted alpha-chromium oxide described above, and said substituted alpha-chromium oxide which has been treated with a fluorinating agent. Such a process is referred to herein as a vapor phase chlorodefluorination reaction. Chlorodefluorination is disclosed in U.S. Patent No. 5,345,017 and U.S. Patent No. 5,763,698 and the teachings of these two patents are hereby incorporated herein by reference.

The chlorodefluorination reactions are typically conducted at temperatures of from about 250°C to 450°C, preferably from about 300°C to about 400°C. The contact time in the reactor is typically from about 1 to about 120 seconds and preferably from about 5 to about 60 seconds. The reactions are most conveniently carried out at atmospheric or superatmospheric pressure.

Chlorodefluorinations involving saturated halogenated hydrocarbons are of particular note. The molar ratio of HCl to the saturated halogenated hydrocarbon compound is typically from about 1:1 to about 100:1, preferably from about 3:1 to about 50:1, and most preferably from about 4:1 to about 30:1. In general, with a given catalyst composition, the higher the temperature, the longer the contact time, and the greater the molar ratio of HCl to saturated halogenated hydrocarbon compound, the greater is the conversion to compounds having lower fluorine content. The above variables can be balanced, one against the other, so that the formation of chlorine-substituted products is maximized.

The product of chlorodefluorination reactions typically comprise unreacted HCl, HF, unconverted starting material, and saturated halogenated hydrocarbon compounds having a lower fluorine content than the starting material by virtue of the substitution of one or more fluorine substituents for chlorine. Specific examples of vapor phase chlorodefluorination reactions which may be carried out using the catalysts of this invention include the conversion of CHF_3 to a mixture of $CHCl_3$, $CHCl_2F$, and $CHClF_2$, the conversion of $CClF_2CClF_2$ to a mixture of

CCl₃CCl₃, CCl₃CCl₂F, CCl₃CClF₂, CCl₂FCCl₂F, CClF₂CCl₂F, and CCl₃CF₃, the conversion of CF₃CClF₂ to a mixture of CCl₃CCl₃, CCl₃CCl₂F, CCl₃CClF₂, CCl₂FCCl₂F, CClF₂CCl₂F, CCl₃CF₃, CClF₂CClF₂, and CF₃CCl₂F, the conversion of CF₃CCl₂CF₃ to a mixture of CF₃CCl₂CClF₂, CF₃CCl₂CCl₂F, CF₃CCl₂CCl₃, and CClF₂CCl₂CCl₃, and the conversion of CF₃CH₂CF₃ to a mixture of CCl₂=CHCF₃ and CCl₂=CClCF₃.

Of note is a catalytic process for producing a mixture containing 1,1-dichloro-3,3,3-trifluoro-1-propene (i.e., CCl₂=CHCF₃ or HCFC-1223za) and 1,1,2-trichloro-3,3,3-trifluoro-1-propene (i.e., CCl₂=CClCF₃ or CFC-1213xa) by the chlorodefluorination of 1,1,1,3,3,3-hexafluoropropane (i.e., CF₃CH₂CF₃ or HFC-236fa) by reaction of HFC-236fa with HCl in the vapor phase in the presence of the catalysts of this invention. The reaction is preferably conducted from about 275°C to about 450°C, more preferably about 300°C to about 400°C with a molar ratio of HCl to HFC-236fa of preferably from about 3:1 to about 20:1. Preferred contacts times are from about 1 second to about 40 seconds. Oxygen in the form of air or co-fed with an inert diluent such as nitrogen, helium, or argon may be added along with the reactants or as a separate catalyst treatment, if desired.

The reaction products obtained by the processes of this invention can be separated by conventional techniques, such as with combinations including, but not limited to, scrubbing, decantation, or distillation. Some of the products of the various embodiments of this invention may form one or more azeotropes with each other or with HF.

The processes of this invention can be carried out readily using well known chemical engineering practices.

Utility

Several of the reaction products obtained through use of the catalysts disclosed herein will have desired properties for direct commercial use. For example, CH₂F₂ (HFC-32), CHF₂CF₃ (HFC-125), CHF₂CF₃ (HFC-125), CH₂FCHF₂ (HFC-134), CF₃CH₂CF₃ (HFC-236fa), and CF₃CH₂CHF₂ (HFC-245fa) find application as refrigerants, CH₂FCF₃ (HFC-134a) and CF₃CHFCF₃ (HFC-227ea) find application as propellants, CH₂FCHF₂ (HFC-134) and CF₃CH₂CHF₂ (HFC-245fa) find application as blowing agents, and CHF₂CF₃ (HFC-125), CF₃CH₂CF₃ (HFC-236fa), and CF₃CHFCF₃ (HFC-227ea) find application as fire extinguishants.

Other reaction products obtained through the use of this invention are used as chemical intermediates to make useful products. For example, CCl_3CF_3 (CFC-113a) can be used to prepare CFC-114a which can then be converted to CH_2FCF_3 (HFC-134a) by hydrodechlorination.

- 5 Similarly, $\text{CF}_3\text{CCl}_2\text{CF}_3$ (CFC-216aa) can be used to prepare $\text{CF}_3\text{CH}_2\text{CF}_3$ (HFC-236fa) by hydrodechlorination and $\text{CF}_3\text{CCl}=\text{CF}_2$ (CFC-1215zc) can be used to prepare $\text{CF}_3\text{CH}_2\text{CHF}_2$ (HFC-245fa) by hydrogenation.

Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following specific embodiments are, therefore, to be construed
10 as merely illustrative, and do not constrain the remainder of the disclosure in any way whatsoever.

EXAMPLES

Catalyst Characterization

- 15 Energy Dispersive Spectroscopy (EDS) and Transmission Electron Microscopy (TEM)

In these studies, the crystallites were analyzed using a Philips CM-20 high-resolution transmission electron microscope operated at an accelerating voltage of 200 kV and configured with an Oxford windowless
20 EDS system with a Si(Li) elemental detector. In the EDS analyses, electron-transparent thin sections of samples were used to minimize sample thickness effects such as fluorescence. Also, due to the similarity of their atomic masses, the X-ray absorption cross-sections for Cr, Co, and Ni were assumed to be the same (see the discussion by Zaluzec on pages
25 121 to 167 in *Introduction to Analytical Electron Microscopy* edited by J. J. Hren, J. I. Goldstein, and D. C. Joy (Plenum Press, New York, 1979). The presence of copper in the EDS of Figures 1, 2, 3, 4, and 5 is due to the TEM grid and background in the microscope.

- 30 X-Ray Absorption Spectroscopy (XAS) and X-Ray Powder Diffraction (XRD)

XRD data were obtained and analyzed according to methods described by Warren in *X-Ray Diffraction* (Addison-Wesley, Reading, MA, 1969). XAS data were obtained at beamline 5BMD, DND-CAT, of the Advanced Photon Source, Argonne National Laboratory. XAS data were
35 obtained and analyzed using the methods described in Koningsberger and Prins in *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES* (John Wiley & Sons, New York, 1988). Spectra were obtained for the K edges of Cr, Co, and Ni. Cr edges were obtained

in transmission geometry, while Co and Ni edges were obtained in fluorescence mode, due to their low concentrations.

Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, under Contract
5 No. W-31-109-Eng-38.

Catalyst Preparation

PREPARATION EXAMPLE 1

Preparation of 95%Chromium/3%Cobalt/2% Nickel Catalyst
(6.2 eq. of excess NH_4NO_3 ; 400°C)

10 A solution of 380.14 g $\text{Cr}(\text{NO}_3)_3[9(\text{H}_2\text{O})]$ (0.95 mole), 8.73 g
 $\text{Co}(\text{NO}_3)_2[6(\text{H}_2\text{O})]$ (0.030 mole), and 5.82 g $\text{Ni}(\text{NO}_3)_2[6(\text{H}_2\text{O})]$ (0.020
mole) was prepared in 1000 mL of deionized water. The solution was
increased from pH 3.1 to pH 8.5 by treatment with 7.4M aqueous
ammonium hydroxide. The slurry was stirred at room temperature for
15 21 hours at pH 8.5. The mixture was then treated with a solution of
472.24 g of $\text{NH}_4(\text{NO}_3)$ (5.90 moles) dissolved in 500 mL of water. The
slurry was stirred for one hour at room temperature and then dried at 110-
120°C in air for about 96 hours. The dried solids was crushed to a powder
and then placed in a covered crucible and calcined at 400°C for 24 hours
20 in air.

Analysis by TEM and EDS indicated the majority of the crystals
were <50 nm in size with uniform incorporation of both cobalt and nickel
into the $\alpha\text{-Cr}_2\text{O}_3$ lattice. No spinel-like phases were detected. Analysis of
the sample by XRD and XAS confirmed that the crystallites had an $\alpha\text{-}$
25 Cr_2O_3 structure and that the average oxidation state of cobalt was 2.89.
The amount of cobalt incorporation in the $\alpha\text{-Cr}_2\text{O}_3$ lattice was about 2.5-
2.7 atom %. XRD confirmed that nickel appeared to be fully incorporated
into the $\alpha\text{-Cr}_2\text{O}_3$ lattice as well.

PREPARATION EXAMPLE 2

30 Preparation of 98%Chromium/1%Cobalt/1% Nickel Catalyst (550°C)
 $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (16.7755 g, 64.6 mmole), and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
(0.1757g, 0.657 mmole), and $\text{Ni}(\text{NO}_3)_2[6\text{H}_2\text{O}]$ (0.1891 g, 0.650 mmole)
were dissolved in deionized water. Aqueous ammonium hydroxide was
then added to the solution until precipitation was complete. The resulting
35 precipitate was filtered and dried in air at 110°C for 12 hours. The
resulting product was ground thoroughly in an agate mortar and then
heated at 550°C in air for 12 hours.

Analysis of the sample by TEM and EDS indicated a small amount of a spinel phase containing cobalt, nickel, and chromium; this phase was richer in cobalt than nickel. The α -Cr₂O₃ phase was present in the form of 100-400 nm crystals; this phase contained both nickel and cobalt with a slight excess of nickel. XAS indicated that cobalt was completely incorporated into the α -Cr₂O₃ lattice. The Ni near edge structure was similar to the composition of PREPARATION EXAMPLE 1 was consistent with some incorporation of nickel into the α -Cr₂O₃ lattice.

PREPARATION EXAMPLE 3

Preparation of 98%Chromium/2%Nickel Catalyst (550°C)
[Cr(NH₃)₆]Cl₃] (16.7727 g, 64.38 mmoles) and Ni(NO₃)₂[6H₂O] (0.3783 g, 1.30 mmoles) were dissolved in deionized water. Aqueous ammonium hydroxide was then added to the solution until precipitation was complete. The resulting precipitate was filtered and dried in air at 110°C for 12 hours. The dried product was then ground thoroughly in an agate mortar and then heated at 550°C in air for 12 hours.

Analysis of the sample by TEM and EDS indicated the presence of a nickel-substituted α -Cr₂O₃ phase mostly in the form of 200 nm crystals; some of the crystals were in the 300-400 nm size range. There was no evidence for a nickel/chromium spinel phase. Some nickel was incorporated into the α -Cr₂O₃ lattice because the Ni near edge structure was similar to the catalyst of PREPARATION EXAMPLE 1.

PREPARATION EXAMPLE 4

Preparation of 98%Chromium/2%Nickel Catalyst (550°C)
Cr(NO₃)₃[9(H₂O)] (50.5 g, 0.126 mole) and Ni(NO₃)₂[6(H₂O)] (0.816 g, 0.00280 mole) were weighed into a porcelain crucible and melted together with stirring in the open air. The mixture was heated to decomposition. A portion of the resulting solid was then calcined in a furnace at 550°C for 12 hours.

In a manner similar to that above, nickel/chromium oxide compositions having the bulk composition 0.5 atom % nickel/99.5 atom % chromium and 1 atom % nickel/99 atom % chromium were prepared and calcined at 550°C.

TEM and EDS analyses of the 98/2 Cr/Ni and the 99.5/0.5 Cr/Ni compositions indicated that these samples contained nickel-substituted crystals of α -Cr₂O₃ ranging in size from 200 to 400 nm. A spinel phase with a Ni/Cr ratio of about 3/1 having crystallite sizes ranging from about 10 to 30 nm was also present especially in the 98/2 Cr/Ni sample.

XAS analysis of these three samples was consistent with nickel incorporation into the α -Cr₂O₃ lattice. The average oxidation state of chromium was about +3.20 with a phase containing a small amount of Cr⁺⁶ also present.

5

PREPARATION EXAMPLE 5

Preparation of 98%Chromium/2%Nickel Catalyst (900°C)

A solution of 392.15 g Cr(NO₃)₃[9(H₂O)] (0.98 mole) dissolved in 1 L of deionized water was treated with 20 mL of a 1 molar solution of aqueous Ni(NO₃)₂[6(H₂O)] (0.020 mole). The resulting solution was treated dropwise with 225 mL of 7.4M aqueous; the pH increased from 1.96 to 8.53 during the addition. The slurry was stirred at room temperature for 24 hours and then evaporated to dryness in air at 110°C and held at that temperature overnight. The dried catalyst was ground to a powder and then calcined in air at 900°C for 20 hours.

15

TEM and EDS analyses indicated that this composition consisted of crystals of α -Cr₂O₃ ranging from about 300 to 400 nm in size with approximately uniform incorporation of nickel.

PREPARATION EXAMPLE 6

Preparation of 95%Chromium/5%Nickel Catalyst (900°C)

20

A solution of 380.14 g Cr(NO₃)₃[9(H₂O)] (0.95 mole) dissolved in 1 L of deionized water was treated with 50 mL of a 1 molar solution of aqueous Ni(NO₃)₂[6(H₂O)] (0.050 mole). The catalyst was treated with aqueous ammonium hydroxide, dried, and calcined as in PREPARATION EXAMPLE 5.

25

PREPARATION EXAMPLE 7

Preparation of 98%Chromium/2%Nickel Catalyst (400°C)

30

A solution of 588.3 g Cr(NO₃)₃[9(H₂O)] (1.47 moles) and 8.72 g (0.030 mole) Ni(NO₃)₂[6(H₂O)] dissolved in 1.5 L of deionized water was treated with 7.4M aqueous ammonium hydroxide until the pH reached 8.5.

35

The addition of ammonium hydroxide took 1.5 hours. The slurry was stirred at room temperature for 24 hours; ammonium hydroxide was added occasionally to keep the pH at about 8.5. The mixture was then evaporated to dryness in air at 110°C over the course of 40 hours. The dried catalyst was ground to a powder and then calcined in air at 400°C for 24 hours.

TEM and EDS analyses indicated that this sample consisted of crystals of α -Cr₂O₃ ranging in size from 20 to 100 nm with approximately

uniform incorporation of nickel. There is no evidence for the formation of a second spinel phase in this sample.

Analysis of the sample by XRD and XAS confirmed that the crystallites had an α -Cr₂O₃ structure. The environment around the Ni atom was very similar to that of the environment around the chromium atoms. The amount of nickel incorporation in the α -Cr₂O₃ lattice was about 1.6 atom %. No spinel phase was observed.

PREPARATION EXAMPLE 8

Preparation of 95%Chromium/5%Nickel Catalyst (400°C)

The procedure of PREPARATION EXAMPLE 7 was repeated using a solution of 760.3 g Cr(NO₃)₃[9(H₂O)] (1.90 moles) and 29.08 g (0.10 mole) Ni(NO₃)₂[6(H₂O)] dissolved in 2 L of deionized water. After the addition of ammonium hydroxide and evaporation at 110°C, the solid was calcined in air at 400°C for 24 hours.

TEM and EDS analyses indicated that this sample consisted of crystals of α -Cr₂O₃ with a much wider particle size range (from 10 to 200 nm) than the composition of PREPARATION EXAMPLE 7 with approximately uniform incorporation of nickel into the alpha-chromium oxide lattice. There was no evidence for the formation of a second spinel phase.

Analysis of the sample by XRD and XAS confirmed that the crystallites had an α -Cr₂O₃ structure. The environment around the Ni atom was very similar to that of the environment around the chromium atoms. The amount of nickel incorporation in the α -Cr₂O₃ lattice was about 2.0 atom %. A small amount of a second nickel-containing phase was observed.

General Procedure for Product Analysis

The following general procedure is illustrative of the method used. Part of the total reactor effluent was sampled on-line for organic product analysis using a gas chromatograph equipped a mass selective detector (GC-MS). The gas chromatography was accomplished with a 20 ft. (6.1 m) long x 1/8 in. (0.32 cm) diameter tubing containing Krytox® perfluorinated polyether on an inert carbon support. The helium flow was 30 mL/min (5.0×10⁻⁷m³/s). Gas chromatographic conditions were 60°C for an initial hold period of three minutes followed by temperature programming to 200°C at a rate of 6°C/minute.

The bulk of the reactor effluent containing organic products and also inorganic acids such as HCl and HF was treated with aqueous caustic prior to disposal.

5 All vapor reactions were conducted at a nominal pressure of one atmosphere.

Legend

	112 is $\text{CCl}_2\text{FCCl}_2\text{F}$	113 is $\text{CCl}_2\text{FCClF}_2$
	113a is CCl_3CF_3	114 is $\text{CClF}_2\text{CClF}_2$
	114a is $\text{CF}_3\text{CCl}_2\text{F}$	115 is CF_3CClF_2
10	214ab is $\text{CF}_3\text{CCl}_2\text{CCl}_2\text{F}$	215aa is $\text{CF}_3\text{CCl}_2\text{CClF}_2$
	215bb is $\text{CCl}_2\text{FCClFCF}_3$	216aa is $\text{CF}_3\text{CCl}_2\text{CF}_3$
	216ba is $\text{CClF}_2\text{CClFCF}_3$	216ca is $\text{CClF}_2\text{CF}_2\text{CClF}_2$
	216cb is $\text{CCl}_2\text{FCF}_2\text{CF}_3$	217ba is $\text{CF}_3\text{CClFCF}_3$
	217ca is $\text{CClF}_2\text{CF}_2\text{CF}_3$	218 is C_3F_8
15	226da is $\text{CF}_3\text{CHClCF}_3$	236fa is $\text{CF}_3\text{CH}_2\text{CF}_3$
	1213xa is $\text{CF}_3\text{CCl}=\text{CCl}_2$	1214 is $\text{C}_3\text{Cl}_2\text{F}_4$
	1215 is C_3ClF_5	13 is CClF_3
	PCE is $\text{CCl}_2=\text{CCl}_2$	

EXAMPLE 9

20 Nickel-substituted chromium oxide (Cr/Ni 98/2 calcined at 400°C, 29.6 g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in PREPARATION EXAMPLE 7, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 88°C to 175°C in a flow of nitrogen

25 (50 cc/min, $8.3 \times 10^{-7} \text{ m}^3/\text{s}$) over the course of about 40 minutes. HF and N_2 were then co-fed to the reactor at flow rates of 50 cc/min ($8.3 \times 10^{-7} \text{ m}^3/\text{s}$) each. After 1.8 hours, the nitrogen flow was decreased to 20 cc/min ($3.3 \times 10^{-7} \text{ m}^3/\text{s}$) and the HF flow increased to 80 cc/min ($1.3 \times 10^{-6} \text{ m}^3/\text{s}$). The reactor temperature was gradually increased to

30 247°C over a 1.6 hour period and then purged with nitrogen (20 cc/min, $3.3 \times 10^{-7} \text{ m}^3/\text{s}$) overnight. The HF treatment was resumed with a flow rate of 80 cc/min ($1.3 \times 10^{-6} \text{ m}^3/\text{s}$) and a nitrogen co-fed at 20 cc/min ($3.3 \times 10^{-7} \text{ m}^3/\text{s}$). These gas flows were maintained for 1.8 hours as the temperature was increased from 249°C to 402°C. The reactor

35 temperature was held at 402°C for 0.5 hour. The nitrogen flow was then shut off and fluorination of CFC-1213xa was begun at 300°C with a 20:1 molar ratio of HF to CFC-1213xa at a contact time of 15 seconds. Under these conditions, the reactor effluent was 94.4 GC area % HCFC-

226da and 4.1% CFC-216aa at 100% conversion of the CFC-1213xa.

Chlorine was then co-fed to the reactor; the molar ratio of HF:CFC-1213xa:Cl₂ was 20:1:4. The composition of the reactor effluent at 350°C is given below.

5	<u>Component</u>	<u>GC Area %</u>
	HCFC-226da	0.7
	CFC-216ba	15.3
	CFC-216aa	55.6
	CFC-217ba	15.8
10	CFC-217ca	0.9
	CFC-215aa	11.1
	CFC-215bb	0.09
	Other	0.6
15	Other products included PCE, CFC-114, CFC-115, FC-218, CFC-1215.	

EXAMPLE 10

Nickel-substituted chromium oxide (Cr/Ni 95/5 calcined at 400°C, 29.2 g, 20 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in PREPARATION EXAMPLE 8, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 68°C to 176°C in a flow of nitrogen (50 cc/min, $8.3 \times 10^{-7} \text{ m}^3/\text{s}$) over the course of about 1 hour. HF and N₂ were then co-fed to the reactor at flow rates of 50 cc/min ($8.3 \times 10^{-7} \text{ m}^3/\text{s}$) each. After 1.3 hours, the nitrogen flow was decreased to 20 cc/min ($3.3 \times 10^{-7} \text{ m}^3/\text{s}$) and the HF flow increased to 80 cc/min ($1.3 \times 10^{-6} \text{ m}^3/\text{s}$). The reactor temperature was gradually increased from 176°C to 402°C over a 3.3 hour period and then held at 400°C for 0.5 hour. The HF flow was then shut off and the reactor purged with nitrogen while it was allowed to cool to 300°C. Fluorination of CFC-1213xa was begun at 300°C with a 20:1 molar ratio of HF to CFC-1213xa at a contact time of 15 seconds. Under these conditions, the reactor effluent was 93.4 GC area % HCFC-226da and 4.9% CFC-216aa at 100% conversion of the CFC-1213xa. Chlorine was then co-fed to the reactor; the molar ratio of HF:CFC-1213xa:Cl₂ was 20:1:4 (15 second contact time). The composition of the reactor effluent at 350°C is given below.

	<u>Component</u>	<u>GC Area %</u>
	HCFC-226da	1.3
	CFC-216ba	25.2
	CFC-216aa	30.1
5	CFC-217ba	18.1
	CFC-217ca	1.0
	CFC-215aa	22.9
	CFC-215bb	0.2
	Other	1.2
10	Other products included CFC-13, CFC-114, CFC-114a, CFC-115, CFC-1215, CFC-216cb, CFC-214ab, PCE.	

EXAMPLE 11

Nickel-substituted chromium oxide (Cr/Ni 98/2 calcined at 900°C, 40.27 g, 25 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in PREPARATION EXAMPLE 5, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 57°C to 175°C in a flow of nitrogen (50 cc/min, $8.3 \times 10^{-7} \text{m}^3/\text{s}$) over the course of about one hour. HF and N₂ were then co-fed to the reactor at flow rates of 50 cc/min ($8.3 \times 10^{-7} \text{m}^3/\text{s}$) each. After 11 minutes, the nitrogen flow was decreased to 20 cc/min ($3.3 \times 10^{-7} \text{m}^3/\text{s}$) and the HF flow increased to 80 cc/min ($1.3 \times 10^{-6} \text{m}^3/\text{s}$). The reactor temperature was gradually increased to 400°C during a 2.7 hour period and maintained at 400°C for an additional hour. At the end of this period, the HF flow was stopped and the reactor cooled to 280°C and purged with under nitrogen overnight. Chlorofluorination of CFC-1213xa was begun at 280°C with HF, CFC-1213xa, and chlorine in molar ratios of 20:1:4 at a contact time of 30 seconds. The composition of the reactor effluent at 340°C is given below.

	<u>Component</u>	<u>GC Area %</u>
30	HCFC-226da	0.8
	CFC-216ba	26.2
	CFC-216aa	25.5
	CFC-216ca	1.1
	CFC-217ba	8.3
35	CFC-215aa	35.3
	CFC-215bb	1.9
	Other	0.9
	Other products included CFC-1215, CFC-217ca	

EXAMPLE 12

Nickel-substituted chromium oxide (Cr/Ni 95/5 calcined at 900°C, 40.27g, 25 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in PREPARATION EXAMPLE 6, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated at 100°C in a flow of nitrogen (50 cc/min, $8.3 \times 10^{-7} \text{m}^3/\text{s}$) for 40 minutes. HF and N₂ were then co-fed to the reactor at flow rates of 50 cc/min ($8.3 \times 10^{-7} \text{m}^3/\text{s}$) each. After 30 minutes, the nitrogen flow was decreased to 20 cc/min ($3.3 \times 10^{-7} \text{m}^3/\text{s}$) and the HF flow increased to 80 cc/min ($1.3 \times 10^{-6} \text{m}^3/\text{s}$). The reactor temperature was then gradually increased to 401°C during a 5 hour period. At the end of this period, the HF flow was stopped and the reactor cooled to 280°C and purged with under nitrogen overnight. Chlorofluorination of CFC-1213xa was begun at 280°C with HF, CFC-1213xa, and chlorine co-fed to the reactor in molar ratios of 20:1:4 at a contact time of 30 seconds. The composition of the reactor effluent at 340°C is given below.

	<u>Component</u>	<u>GC Area %</u>
	HCFC-226da	1.1
	CFC-216ba	23.7
20	CFC-216aa	19.2
	CFC-216ca	1.2
	CFC-217ba	11.9
	CFC-215aa	29.9
	CFC-215bb	12.0
25	Other	0.3
	Other products included CFC-1215, CFC-1214.	

EXAMPLE 13

A mixed nickel- and cobalt-substituted chromium oxide (Cr/Co/Ni 95/3/2, 26.37g, 19 mL, -12 to +20 mesh, (1.68 to 0.84 mm)), prepared as described in PREPARATION EXAMPLE 1, was placed in a 5/8" (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The catalyst was heated from 81°C to 175°C in a flow of nitrogen (50 cc/min, $8.3 \times 10^{-7} \text{m}^3/\text{s}$) over the course of about one hour. HF and N₂ were then co-fed to the reactor at flow rates of 50 cc/min ($8.3 \times 10^{-7} \text{m}^3/\text{s}$) each. After 0.3 hour, the nitrogen flow was decreased to 20 cc/min ($3.3 \times 10^{-7} \text{m}^3/\text{s}$) and the HF flow increased to 80 cc/min ($1.3 \times 10^{-6} \text{m}^3/\text{s}$). The reactor temperature was gradually increased to 400°C during a 3.6 hour period. The HF flow was then stopped and the reactor cooled to

298°C under 20 sccm ($3.3 \times 10^{-7} \text{ m}^3/\text{s}$) nitrogen flow. Chlorofluorination of CFC-1213xa began at 300°C with HF, CFC-1213xa, and chlorine were co-fed to the reactor in molar ratio of 20:1:4, respectively, at a contact time of 15 seconds. The GC-MS analyses of the reactor effluent at 320°C (molar feed ratio of 20:1:4) and 375°C (molar feed ratio of 30:1:2) is given below.

		<u>GC Area %</u>	
		<u>320°C</u>	<u>375°C</u>
10	<u>Component</u>		
	HCFC-226da	1.4	1.0
	CFC-216ba	21.2	16.3
	CFC-216aa	22.0	40.8
	CFC-217ba	16.6	34.0
	CFC-215aa	35.9	5.0
15	CFC-217ca	0.7	1.9
	CFC-216cb	1.0	-
	Other	1.2	

Other products included CFC-1215, CFC-114, CFC-114a, HCFC-225da, CFC-113.

CLAIMS

What is claimed is:

1. A crystalline alpha-chromium oxide where from about 0.05 atom % to about 2 atom % of the chromium atoms in the alpha-chromium oxide lattice are substituted by nickel atoms, and optionally, additional chromium atoms in the alpha-chromium oxide lattice are substituted by trivalent cobalt atoms, provided that the total amount of the nickel atoms and the trivalent cobalt atoms in the alpha-chromium oxide lattice is no more than 6 atom %.
2. A chromium-containing catalyst composition comprising as a chromium-containing component the crystalline substituted alpha-chromium oxide of Claim 1.
3. A chromium-containing catalyst composition comprising a chromium-containing component prepared by treating the crystalline substituted alpha-chromium oxide of Claim 1 with a fluorinating agent.
4. A process for changing the fluorine distribution in a hydrocarbon or a halogenated hydrocarbon in the presence of a catalyst, characterized by:
 - using as the catalyst a composition comprising at least one chromium-containing component selected from the group consisting of the crystalline substituted alpha-chromium oxide of Claim 1 and a crystalline substituted alpha-chromium oxide of Claim 1 which has been treated with a fluorinating agent.
5. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound or an unsaturated hydrocarbon compound is increased by reacting said compound with hydrogen fluoride in the vapor phase in the presence of said catalyst composition.
6. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound or a hydrocarbon compound is increased by reacting said compound with HF and Cl₂ in the vapor phase in the presence of said catalyst composition.
7. The process of Claim 4 wherein the fluorine distribution in a halogenated hydrocarbon compound is changed by isomerizing said halogenated hydrocarbon compound in the presence of said catalyst composition.
8. The process of Claim 4 wherein the fluorine distribution in a halogenated hydrocarbon compound is changed by disproportionating said

halogenated hydrocarbon compound in the vapor phase in the presence of said catalyst composition.

9. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound is decreased by dehydrofluorinating said halogenated hydrocarbon compound in the presence of said catalyst composition.

10. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound is decreased by reacting said halogenated hydrocarbon compound with hydrogen chloride in the vapor phase in the presence of said catalyst composition.

11. A method for preparing a composition comprising the crystalline substituted alpha-chromium oxide of Claim 1, comprising:

- (a) co-precipitating a solid by adding ammonium hydroxide to an aqueous solution of a soluble divalent nickel salt, a soluble trivalent chromium salt, and optionally, a soluble divalent or trivalent cobalt salt, that contains at least three moles of nitrate per mole of chromium in the solution, has a nickel concentration of from about 0.05 mole % to about 2 mole % of the total of nickel, chromium, and cobalt (if present) in the solution, and has a combined concentration of nickel and cobalt (if present) of no more than 6 mole % of the total of nickel, chromium, and cobalt (if present) in the solution; and after at least three moles of ammonium per mole of chromium has been added to the solution;
- (b) collecting co-precipitated solid formed in (a);
- (c) drying the collected solid; and
- (d) calcining the dried solid.

12. The method of Claim 11 wherein the soluble nickel salt is a nitrate or a hydrated nitrate.

13. The method of Claim 12 wherein the soluble chromium salt is a nitrate or a hydrated nitrate.

14. The method of Claim 13 wherein more than three moles of ammonium nitrate per mole of chromium is present in the aqueous solution.

1/8

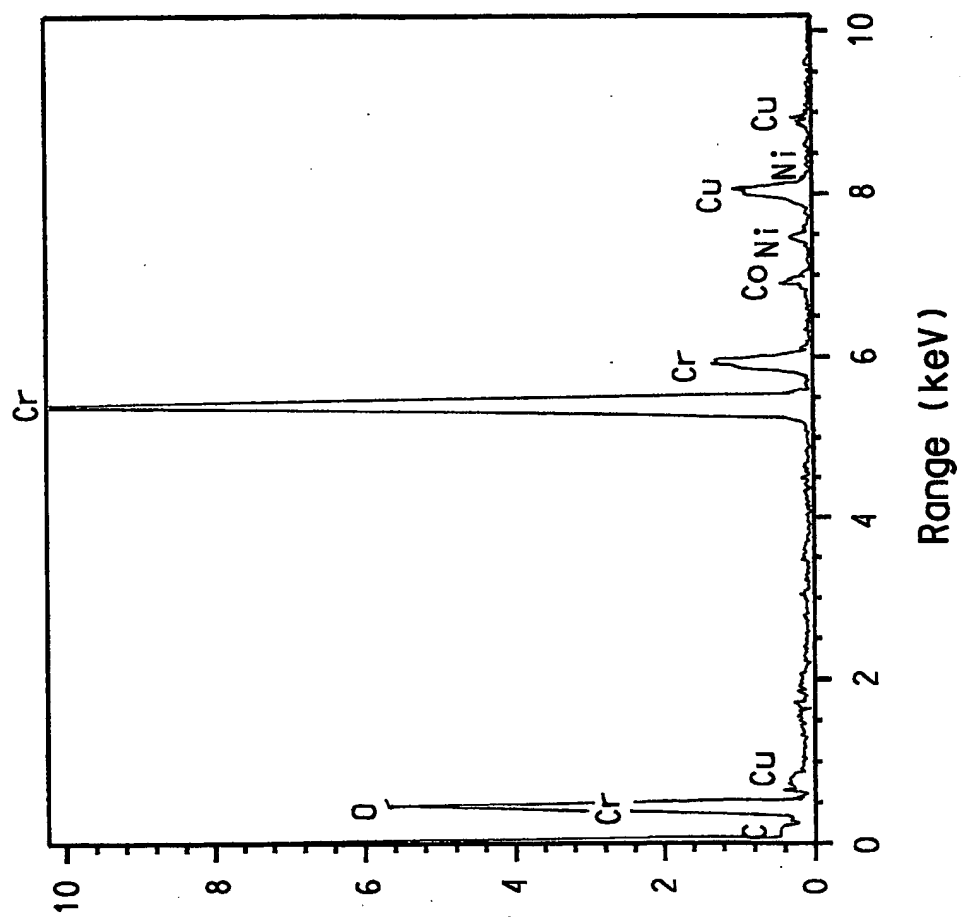


FIG. 1

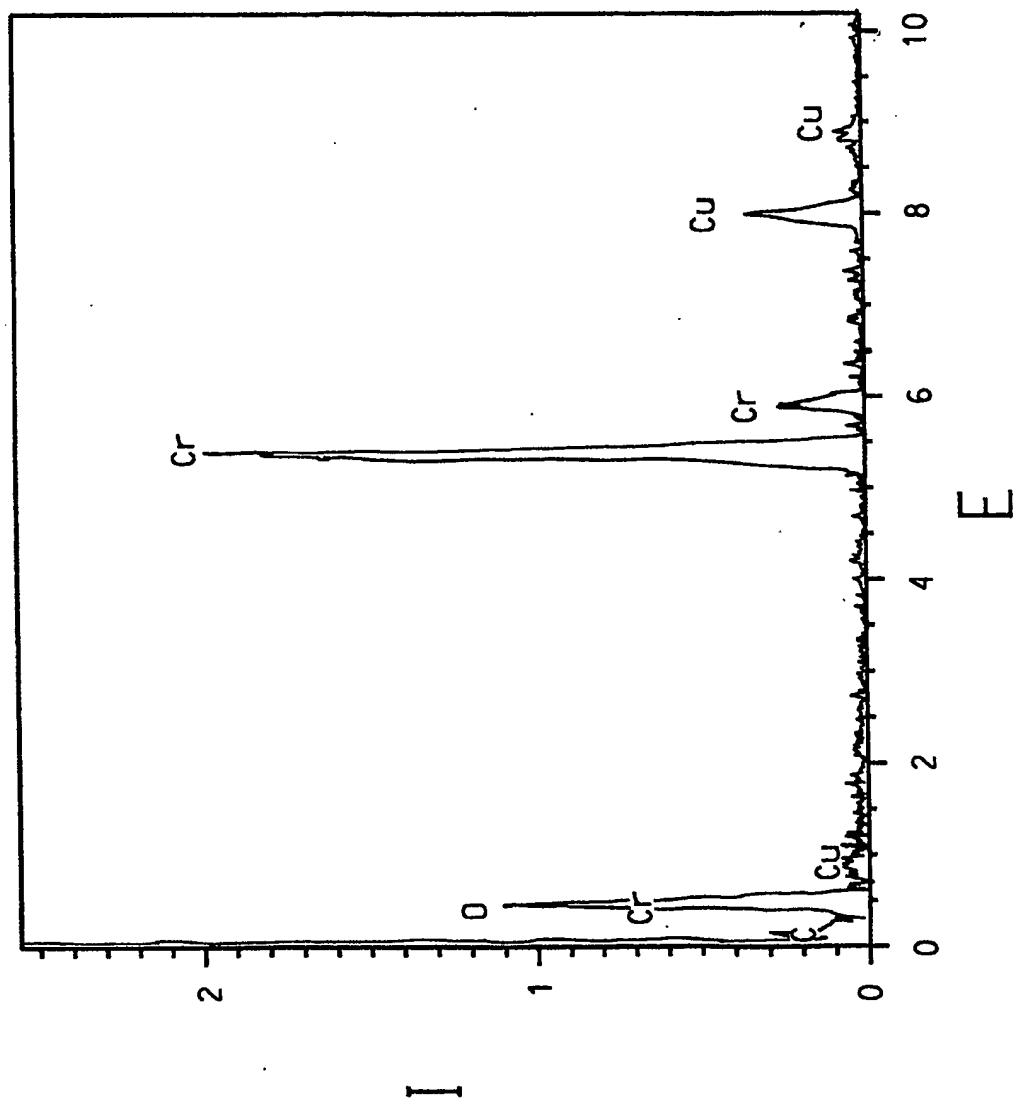


FIG. 2

3/8

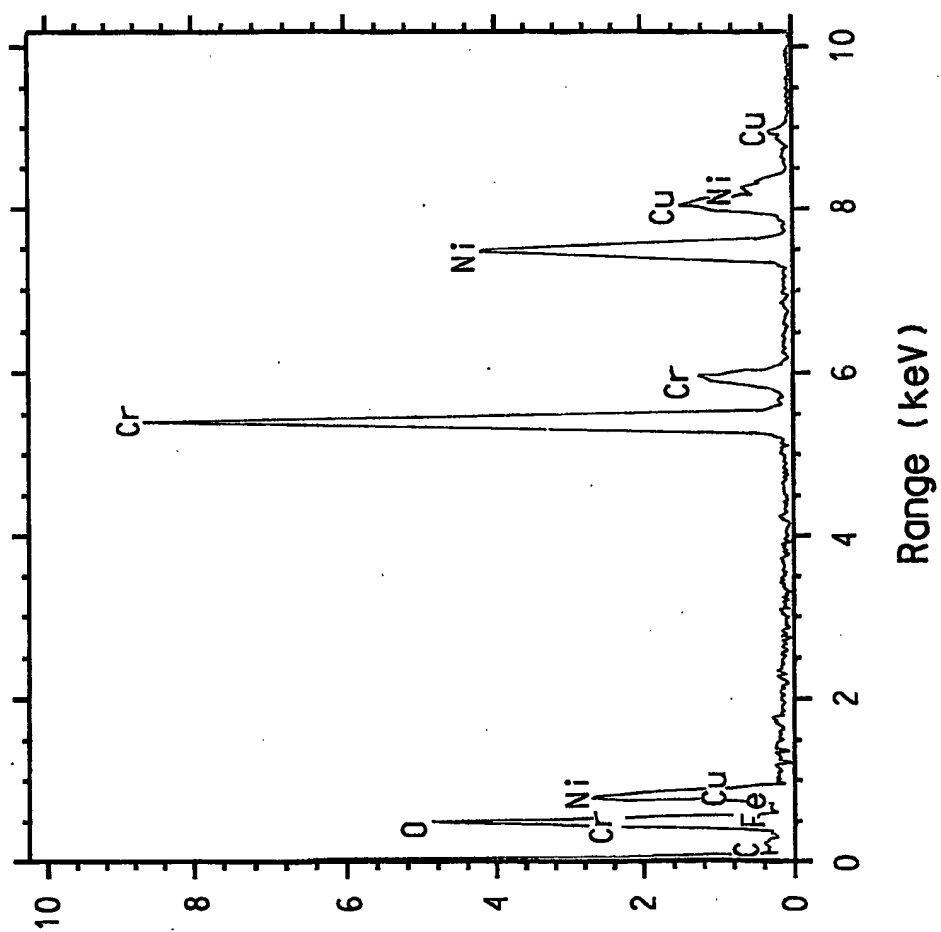


FIG. 3

4/8

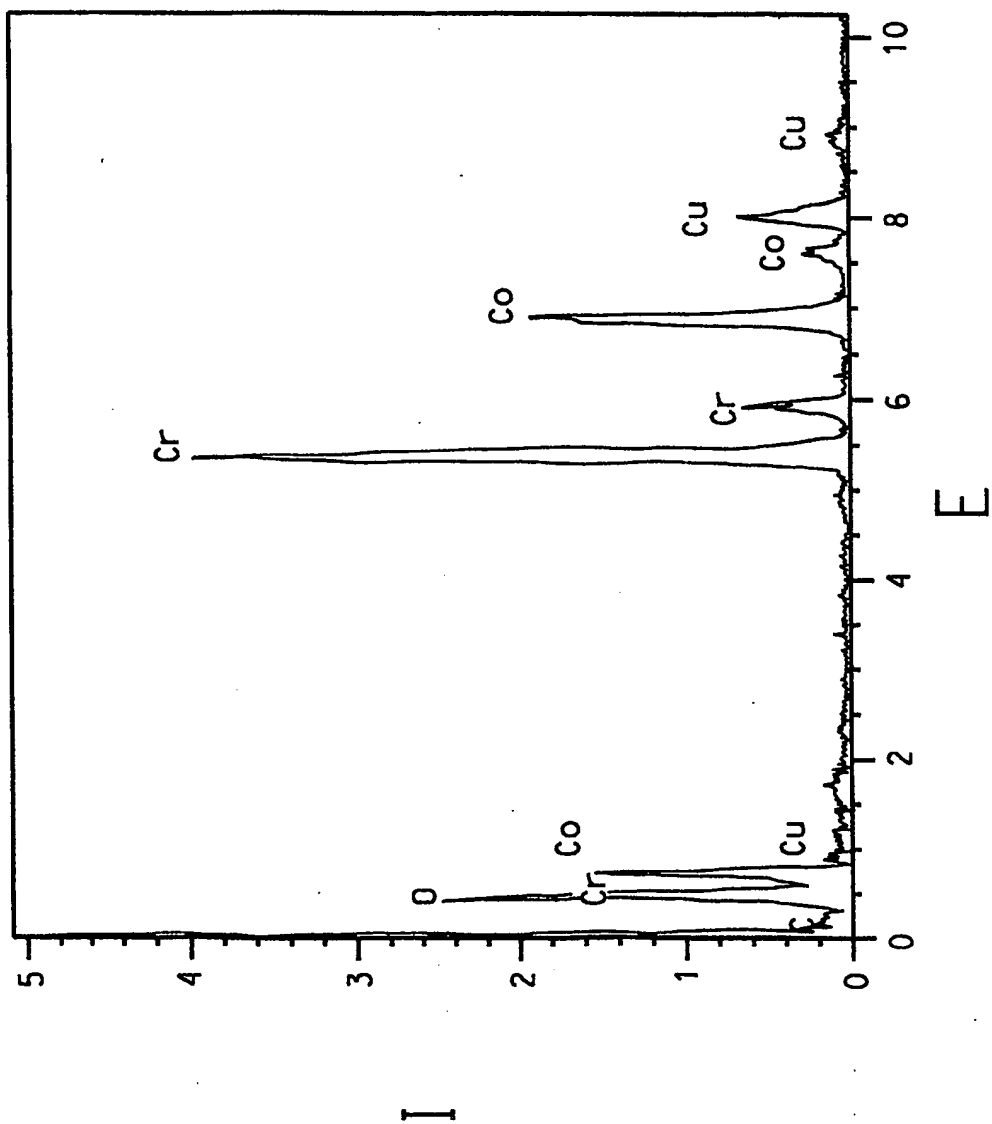


FIG. 4

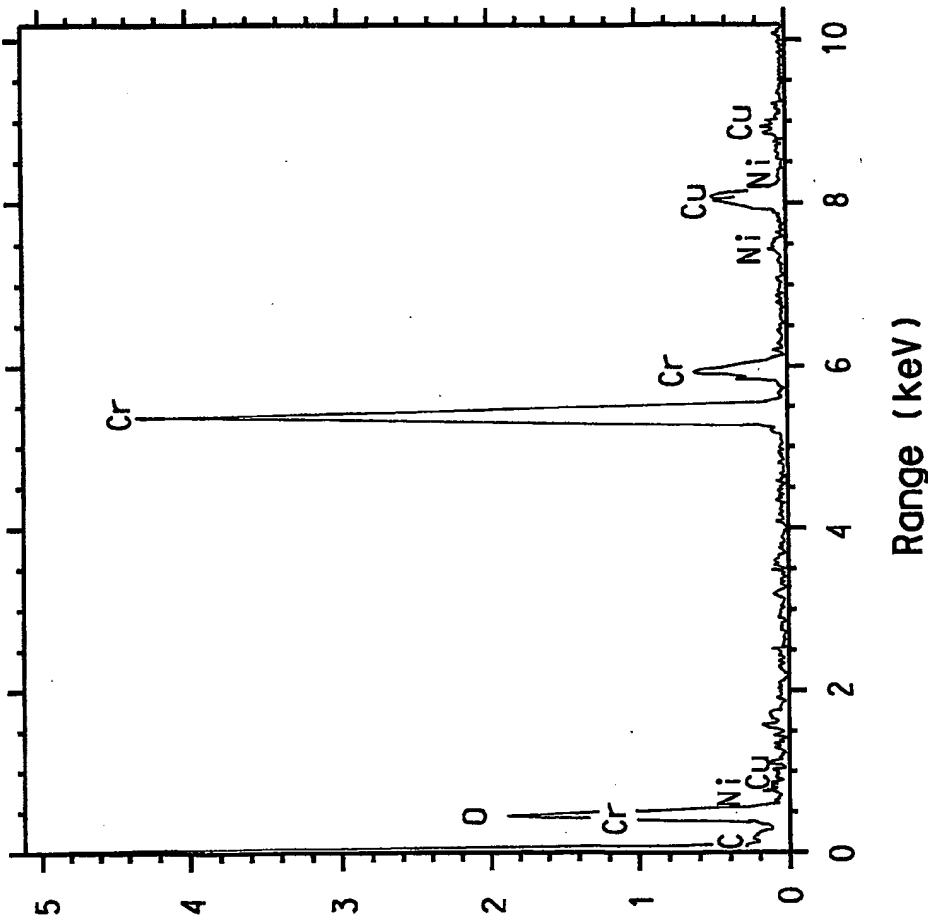


FIG. 5

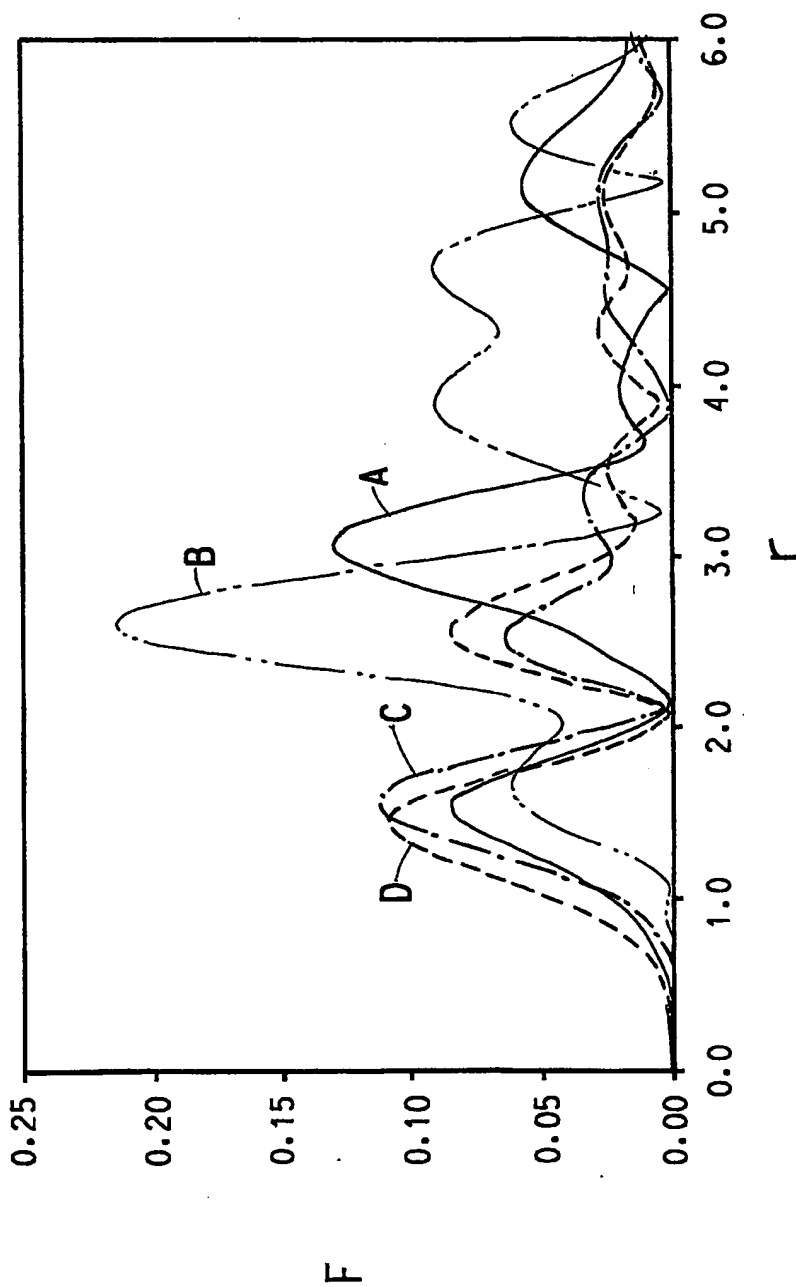


FIG. 6

7/8

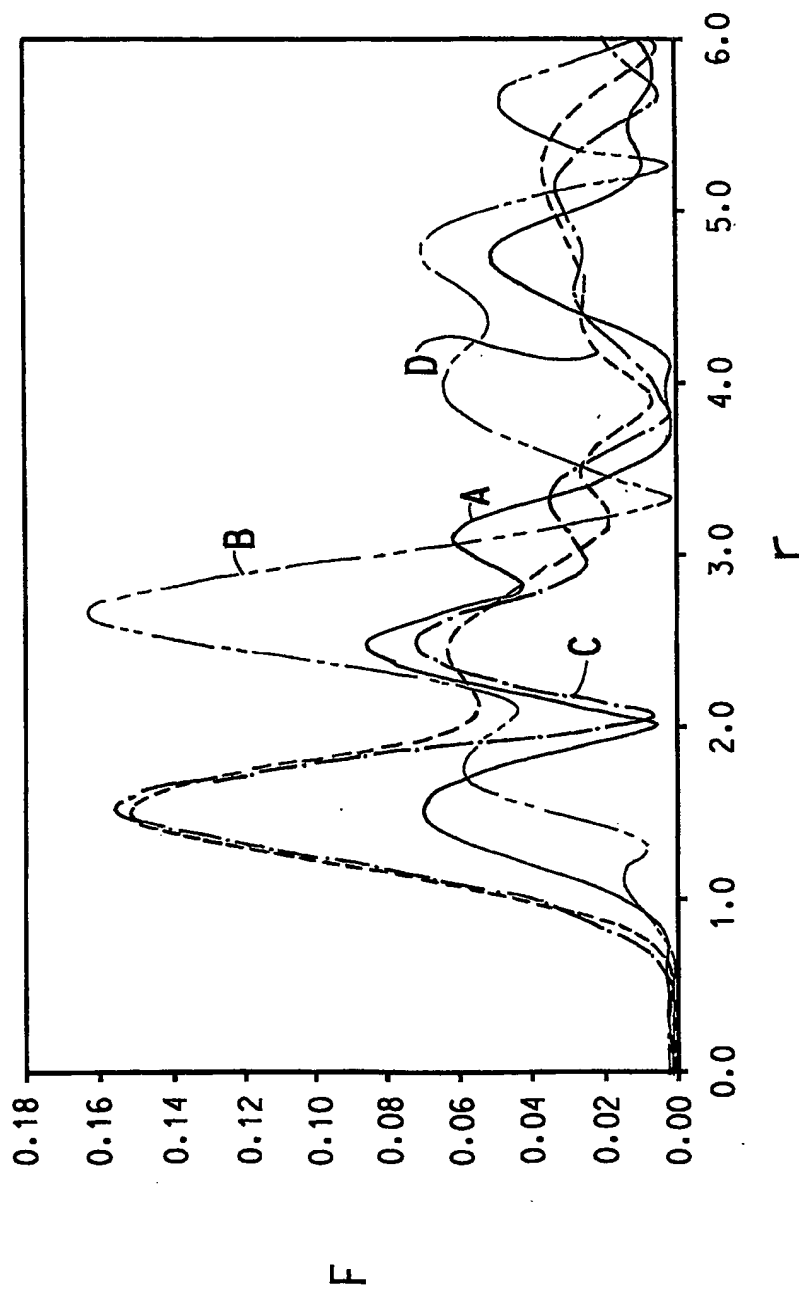


FIG. 7

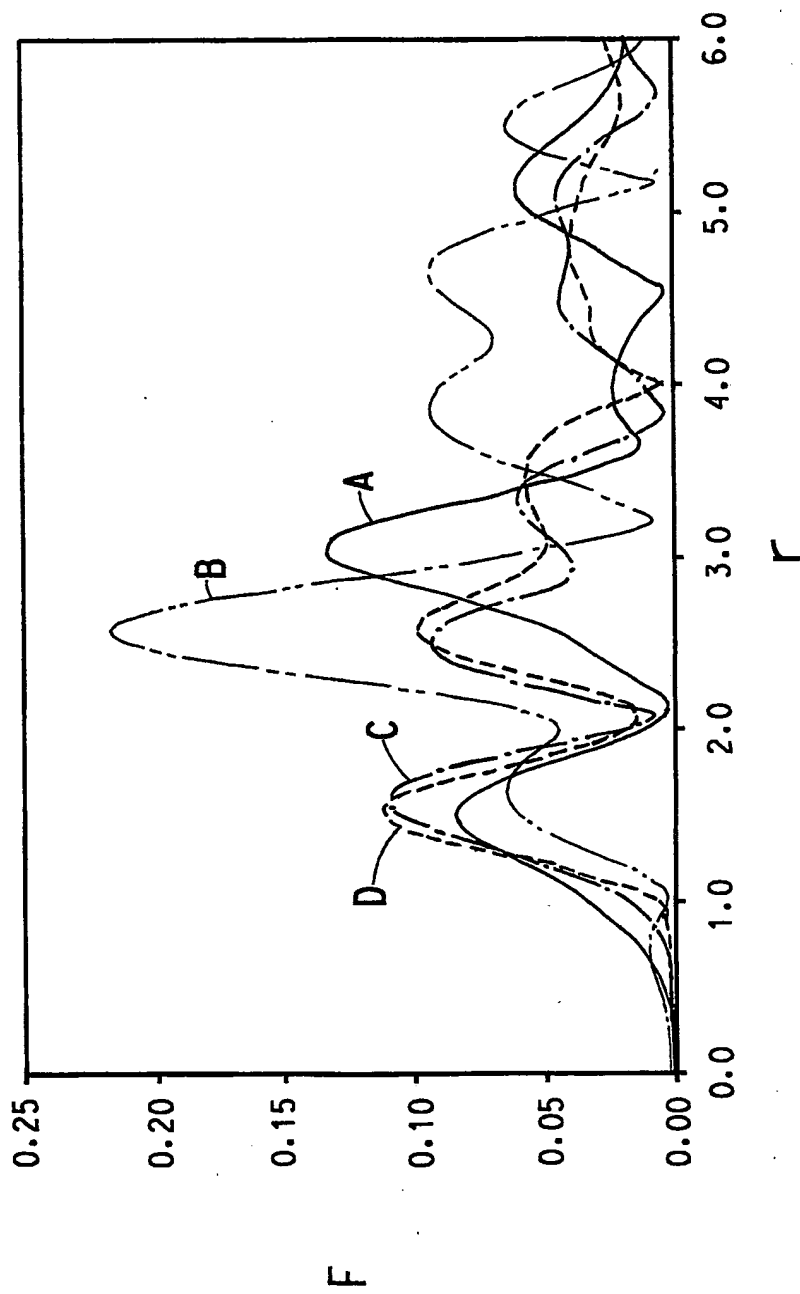


FIG. 8

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US 03/26327

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/86 B01J23/26 C07C17/20 C07C19/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 847 801 A (ATOCHÉM ELF SA) 17 June 1998 (1998-06-17) page 2, line 47 - page 3, line 37 examples claims 1,6,8-17	1-14
X	US 2002/006374 A1 (KOURTAKIS KOSTANTINOS ET AL) 17 January 2002 (2002-01-17) examples 19,20	1,2, 11-14
X	US 3 804 778 A (SALINDRES R) 16 April 1974 (1974-04-16) column 2, line 10 - line 41 column 3, line 50 - line 63 examples claims 1,3	1-14



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 December 2003

Date of mailing of the international search report

26/01/2004

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Schoofs, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/26327

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 546 883 A (ATOCHM ELF SA) 16 June 1993 (1993-06-16) page 3, line 1 - line 3 page 3, line 4 - page 4, line 18 page 4, line 43 - line 56 examples claims 1,12,13 page 5, line 16 - line 20	1-14
X	& AU 29972 92 A 10 June 1993 (1993-06-10) cited in the application -----	
A	US 5 185 482 A (MANZER LEO E) 9 February 1993 (1993-02-09) cited in the application examples claims 1,7 -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/26327

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0847801	A	17-06-1998	FR 2757085 A1	19-06-1998
			AU 4831797 A	18-06-1998
			CA 2222325 A1	13-06-1998
			CN 1191157 A ,B	26-08-1998
			EP 0847801 A1	17-06-1998
			JP 10180104 A	07-07-1998
			US 2002155947 A1	24-10-2002
US 2002006374	A1	17-01-2002	AU 1458101 A	06-06-2001
			AU 3836001 A	27-08-2001
			CA 2389802 A1	17-05-2001
			CA 2400046 A1	23-08-2001
			EP 1232115 A1	21-08-2002
			EP 1257497 A2	20-11-2002
			WO 0134517 A1	17-05-2001
US 3804778	A	16-04-1974	WO 0160740 A2	23-08-2001
			FR 2135473 A5	22-12-1972
			BE 782946 A1	03-11-1972
			CA 982594 A1	27-01-1976
			CH 542653 A	15-10-1973
			DE 2221849 A1	16-11-1972
			ES 402318 A1	16-03-1975
EP 0546883	A	16-06-1993	GB 1329797 A	12-09-1973
			IT 957714 B	20-10-1973
			NL 7205750 A ,B,	08-11-1972
			FR 2684567 A1	11-06-1993
			AU 662185 B2	24-08-1995
			AU 2997292 A	10-06-1993
			CA 2084864 A1	10-06-1993
EP 0546883	A	16-06-1993	DE 69204147 D1	21-09-1995
			DE 69204147 T2	11-04-1996
			EP 0546883 A1	16-06-1993
			ES 2075656 T3	01-10-1995
			GR 3017922 T3	31-01-1996
			JP 2059670 C	10-06-1996
			JP 5269382 A	19-10-1993
US 5185482	A	09-02-1993	JP 7071635 B	02-08-1995
			KR 9605494 B1	25-04-1996
			US 5523500 A	04-06-1996
			US 5345016 A	06-09-1994
			AT 130593 T	15-12-1995
			AU 622295 B2	02-04-1992
			AU 5164990 A	24-08-1990
US 5185482	A	09-02-1993	BR 9007059 A	12-11-1991
			CA 2009189 A1	03-08-1990
			CN 1045091 A	05-09-1990
			DE 69023759 D1	04-01-1996
			DE 69023759 T2	20-06-1996
			EP 0455748 A1	13-11-1991
			ES 2080139 T3	01-02-1996
US 5185482	A	09-02-1993	JP 2695042 B2	24-12-1997
			JP 4503215 T	11-06-1992
			MX 170803 B	15-09-1993
			RU 2034822 C1	10-05-1995
			WO 9008755 A1	09-08-1990

INTERNATIONAL SEARCH REPORT
information on patent family members

International Application No
PCT/US 03/26327

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5185482	A	ZA 9000802 A	30-10-1991